

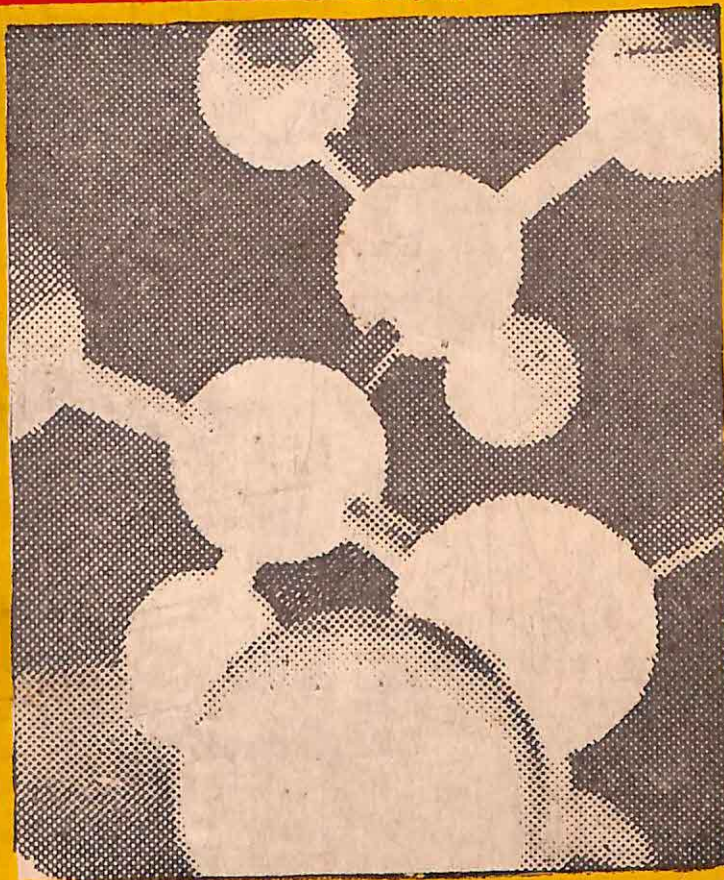
Essentials of Chemistry

Vol. I

V.C. GARG

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P.C. JAIN



PITAMBAR PUBLISHING COMPANY

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ESSENTIALS OF CHEMISTRY

(Vol. I for Class XI)

Dr. V. C. GARG

By

P. C. JAIN

Department of Chemistry
Delhi College of Engineering,
Delhi.



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PREFACE

In the present book an attempt has been made to present the whole course of the subject prescribed for the Senior School Certificate Examination, 1980 onward for Class XI of the Central Board of Secondary Education, New Delhi, under the New 10+2 Scheme.

Generally, students face a lot of difficulty in effectively grasping the basic principles of the subject from majority of text books available in the market. This book has been written entirely from the students angle and the whole subject has been presented in a simple, lucid and comprehensive manner. We have tried to arrange, as suitably as we could, the different aspects of the subject in a systematic and well-knit style. Moreover, every effort has been made to introduce modern concepts in an intelligible form with the aid of large number of conceptual diagrams, illustrative figures, etc. Some of the special features of this book are :

- (1) Simple and clear presentation.
- (2) Easily intelligible language.
- (3) Illustrations with neat diagrams.
- (4) Various theories explained step by step.
- (5) Solved examples and sufficient number of exercises are given at proper places.
- (6) Modern concepts of "mechanisms of reactions" have been discussed, wherever necessary.
- (7) Various sub-heads and important notes have been incorporated to facilitate students to remember various points more easily.
- (8) Large number of questions—long answer type, short answer type, objective type and problems have been given at the end of each chapter. This will enable the students to test their understanding and finally sharpen their wits.
- (9) Fundamental ideas have been explained on modern lines in a coherent manner.
- (10) Modern terms and notations have been used throughout the book.

We are sure, the book will prove to be quite useful for the students, whom it is meant for. Of course, the extent to which we have succeeded in doing justice to the project can be judged only by the readers. We, on our part, will be ever-ready to receive with gratitude any suggestions that are intended to improve the warp and woof of this book.

—Authors

Syllabus in Chemistry

(Prescribed by the Central Board of Secondary Education,
New Delhi)

CLASS XI

(100 Marks)

One Theory Paper

3 Hours

70 Marks

One Practical

3 Hours

30 Marks

THEORY

Structure and Scope of Chemistry

Role of Chemistry in modern life in Indian context (This part includes historical account also).

Atoms

5

Mole concept, Bohr model-line spectra (a brief idea). Inadequacy of Bohr's model. Concept of an orbital, quantum numbers (only mention of quantum numbers and its application to electronic structure of atoms). Pauli's exclusion principle, Aufbau principle. Stability of filled and half filled orbitals (with respect to energy in a qualitative manner) Shapes of *s* and *p* orbitals. Configuration of transition elements in 3rd series.

Periodic Properties of Elements

5

Periodic law, long form periodic table. Periodicity in properties like atomic radii and volume, ionic radii, ionization energy, electron affinity. Division of elements into *s*, *p*, *d* and *f* blocks.

Chemical Bonds and Molecules

7

Concept of orbital overlap in bond formation, sigma and pi bonds, hybridization (sp^1 sp^2 sp^3) properties of covalent compounds, shapes of simple molecules like H_2O , NH_3 , CO_2 , CH_4 , SO_2 , C_2H_4 and C_2H_2 . Coordinate bond formation with a few examples. Ionic, bonds : definition, factors influencing the formation of ionic compounds. An elementary treatment of metallic and hydrogen bonds.

Chemical Energetics

4

Exothermic and endothermic reaction. Enthalpies of formation, combustion, neutralization reaction, solution, fusion, vaporization and sublimation, Hess's law. Claorific values of foods and fuels.

Chemical Equilibrium

5

Law of mass action and its application to chemical equilibrium. Le Chatelier-Braun Principle, factors influencing

Ionic equilibrium in aqueous solutions : solubility product and their application in qualitative analysis. Common ion effect Bronsted and Lowry's concept of acids and bases acid base equilibria, ph hydrolysis of salts, buffer solutions.

Electro Chemistry

4

Electrolysis, Faraday's laws and calculations based on them. Application of electrolysis to electroplating, Electrolytic conduction (specific, equivalent and molar conductances). Kohlrausch's law. Concept of strong and weak electrolytes based on these.

Hydrogen

2

Its unique position in the periodic table. Electro-positive and electro-negative characters.

Water and Hydrogen Peroxide

3

Heavy water, production by electrolysis, importance of heavy water in nuclear chemistry, Hydrogen peroxide, properties and uses.

Alkali Metals (Group IA Elements)

3

A general treatment, electronic structure and general trends in properties.

Important minerals, electrolytic method of extracting alkali metals. Uses of sodium, manufacturing principles of uses of sodium hydroxide, sodium carbonate sodium bicarbonate, potassium cyanide and potassium chlorate.

Alkaline Earth Metals (Group II Elements,

2

Important Ores from which metals are extracted generally Preparation of alkaline earth metals, important compounds oxides, carbides sulphates.

Boron and aluminium (Group III Elements)

3

General trends in properties of the elements of boron family. Important ores of boron. Preparation and uses of borax orthoboric acid, aluminium chloride and alums. Extraction of Aluminium from bauxite and its uses.

The Carbon family (Group IVA Elements)

3

General trends in properties, important ores of tin and lead, preparation and uses of white lead, a chrome yellow, oxides of lead, lead tetraethyl. Alloys of tin and lead.

The Nitrogen Family (Group VA Elements)

3

General trends, in properties of the family, important Minerals of phosphorus. Manufacture of ammonia and nitric Acid. (spatial and resonance formula to be avoided) chemical fertilizers (N.P.K.).

Introduction to carbon compounds ; Hydrocarbons 4

Organic chemistry as chemistry of carbon compounds, hydrocarbons, their types, homologous series :

- (a) Alkanes ; sp^3 hybridization, sigma bond, tetrahedral structure, free rotation about sigma bond, chain isomerism.
- (b) Alkanes : sp^2 hybridization, carbon-carbon double bond, sigma and pi bonds. Planar molecule of ethylene.
- (c) Alkenes : Sp -hybridization, carbon-carbon triple bond linear molecule of acetylene.
- (d) Arenes : Delocalization of electrons in benzene : o.m p isomers.
- (e) systematic nomenclature : Compounds having carbon atoms upto six to be discussed.

Sources and Synthesis of Hydrocarbons 5

Process in petroleum, industry, pyrolysis of coal, common laboratory preparations of alkenes, alkenes and alkynes.

Properties and reactions of Hydrocarbons 8

Change in physical properties with chain length, Chemical properties, combustion and controlled oxidation, free radicals halogenation and cracking in alkanes. Catalytic hydrogenation in alkenes and alkynes. Markwnikoff's rule. Reactions of arenes (mechanisms not required).

Purification and characterization of organic compounds 4

Purification (crystalization, sublimation, distillation, differential extraction and chromatography). Qualitative analysis of elements. Calculation of empirical and molecular formulae, from weight percentage data of elements.

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Chapter 5 of Part I has been omitted from the latest syllabus of CBSE.

PART I—PHYSICAL

1

Nature and Scope of Chemistry

1.1. INTRODUCTION

Earliest history records human interest in many natural phenomena such as fire, lightning and thunder, as well as concern with common things like air, water and soil, and with the sun, moon, and stars. For thousands of years people struggled to find a way to describe such things, in terms of simpler substances. In their early attempts, superstitions, black magic and religious dictums played a major role. For a long period of time, many people lived under the beliefs that :

The earth was the centre of the universe.

The four elements were air, fire, earth and water.

A philosopher's stone could change base metal to gold.

Life developed by spontaneous generation.

Chemistry developed from two sources—one philosophical, the other utilitarian. Greek philosophers sought to account for the material diversity of the world in orderly and intellectually satisfying terms. However, practical men and women of the several ancient civilizations expanded arts and crafts into many useful technologies for making glass, smelting and alloying metals, compounding medicine, etc. Greek philosophers attempted to explain phenomena like transformation of wood into ash, grass to milk, seed to growing plants, etc., in terms of four elements. Some said that substances were made up of continuous masses. They also sought reasonable, even mathematical, explanations for the observed behaviour of matter. However, the Greeks failed to understand the necessary connection between the creations of their minds and the applications of these in everyday life.

Meanwhile, association of the metallic arts with the Egyptian priesthood gave rise to the mysticism known as the period of

1.2 | ESSENTIALS OF CHEMISTRY

Alchemy. Alchemy was developed by Arabic cultures between 600 A.D. and 1000 A.D. They were largely concerned with the transmutation of base metals into gold. Alchemy flourished until the early 18th century, having in the mean time given rise to a school that emphasized the role of chemistry in the cure of diseases (the **iatrochemists**). In their search for transmutation process, Alchemists discovered a great many useful facts.

The early Chinese were much more practical than the Greeks. Salt and wine were prepared in China before 1100 B.C. A form of Alchemy began about 400 B.C. and flourished at least until late in the 13th century A.D. The principal aim of Chinese Alchemists was to prepare *chintan*, a medicine for prolonging life. Their other endeavours led to the preparation of porcelain and paper (in about 200 B.C.) and gun powder (in about 500 A.D.). Moreover, the early Chinese believed in the existence of two fundamental elements *yin* and *yang*, and they thought that these two elements react in different amounts with other objects that produced various kinds of chemicals.

Knowledge about nature grew gradually, but as it became organized and refined, and the quest to know the universe became known as science. Science may be defined as describing, creating and understanding facts of human experience—(Lindsey). It would be well nigh impossible to achieve this object unless we evolve a system to study the countless natural phenomena. Hence, it would be better to say that science is an activity pursued by means of the scientific methodology.

1.2. SCIENTIFIC METHOD

The world around us presents an extraordinary variety of different forms of matter, but we now know a great deal about the way in which matter is constituted and how it will behave under different conditions. This is the result of applying the scientific method. The steps in the scientific procedures may be outlined as follows.

The first aim of a scientist, when investigating any problem, is to discover the facts, and this is usually done by carrying out experiments. If a large number of experiments all give similar results, it is possible to summarise the results into a single statement, which is then known as *law*. Thus, '*law*' is a concise statement summarising the results of a large number of separate experiments all leading to the same conclusion.

Once a law has been enunciated, and checked by further experimental work, efforts are made to account for the law. This is done by putting forward a **hypothesis**, which is an idea or a collection of ideas, able to account for the facts. These first ideas are generally somewhat tentative, but if they become widely accepted as true after consideration, discussion and modification, they are then restated in what is called a '**theory**'.

Finally, if a theory can be build up which effectively accounts for a variety of facts, it is often possible to use it to predict some new experimental results or facts. The theory can then be used and developed. For example, the "kinetic theory of gases" is a plausible explanation of how gases behave and from it can be predicted most of the observed gaseous phenomena. The actual, or final, proof of a theory is, in most cases, an impossibility. Thus, scientists are certain that the atomic theory is essentially correct, but its actual proof has never been completely accomplished.

1.3. THE SCIENCE OF CHEMISTRY

Such forms of matter as wood and glass, water and gasoline, salt and sugar, coal and granite, and iron and gold differ strikingly from each other in many properties. These differences in properties occur as a result of differences in the composition and structure of the various substances. In our study of chemistry, we shall be concerned with the composition and structure of matter. This is not the whole story of chemistry, however, for matter is not static. Much of our existence, in fact, depend upon the changes which occur in matter. What changes in matter are taking place when iron rusts, milk sours, a storage battery produces an electric current, and food is digested and assimilated by the body? As we proceed in our study of chemistry, we shall look into the change in the composition and structure of matter, the causes which produce these chages, the changes in energy accompanying them, and the principles and laws involved in these changes. In brief, then the science of chemistry "is the study of the composition, structures and properties of matter, and the changes which it undergoes."

What we now consider to be "modern chemistry" began with investigations of gases under pressure and vacuum (a disciple then called "*pneumatics*") in the 17th century by Evangelista Torricelli, Blaise Pascal, Otto Von Guericke and Robert Boyle. These studies led to improvements in laboratory techniques that helped another generation of scientists (notably Karl Wilhelm Scheelem, Henry Cavendish, Joseph Priestley and Antoino Lavoiser), about a century later, to formulate a quantitative basis for chemical changes, especially combustion and other reactions involving oxygen. These advances, in turn, set the stage for the chemical pioneers of the 19th century (John Dalton, Amadeo Avogadro, Jons Jakob Berzelius, and Stanislao Cannizzaro) to interpret chemical changes in terms of atoms and molecules, and to devise rational systems of atomic and molecular weights. The latter half of that century witnessed a very fruitful growth of systematizing conecepts—the periodic table, the structural theory of organic chemistry, and stereochemistry (the geometry of molecules). In 1896, Henri Becquerel discovered radioactivity, thus initiating a new chain of discoveries that led to a great refinement of our ideas about the atom, and to new understanding of chemical processes. It is to these ideas that we shall turn to provide the major conceptual frame work to our study of chemistry.

1.4 | ESSENTIALS OF CHEMISTRY

The science of chemistry has become so vast during the last century that chemists usually specialize in one of several principal branches like,

(1) *Analytical chemistry is concerned with the identification, separation, and quantitative determination of composition of different substances.*

(2) *Physical chemistry is primarily concerned with the structure of matter, energy changes, and laws, principles and theories which explain the transformations of one form of matter into another.*

(3) *Organic chemistry is the branch dealing with the compounds of carbon.*

(4) *Inorganic chemistry is concerned with the chemistry of the elements other than carbon and their compounds.*

(5) *Biochemistry is the chemistry of the substances comprising living organisms, plants and animals.*

1.4. CHEMISTRY IN THE SERVICE OF MANKIND

Modern science, including chemistry, is constantly providing us with a supply of new things for better living, for a longer and healthier life, and an increased leisure in which to enjoy life. From the laboratory of the research chemists have come such familiar substances as penicillin, streptomycin, vitamins, hormones, and sulphadiazine to conquer disease and to save and prolong life. The modern automobiles and airplanes have become possible through the production of special alloys, high octane fuels, and synthetic rubber and other plastics. Synthetic fibers such as nylon, dacron, polyester and cashmilon are competing with cotton and wool; while plastics and new types of glass are replacing steel, wood, bone, cork, and ceramics in an ever increasing number of applications. An increased production of foodstuffs to keep abreast our rapidly growing population has been made possible by the development, production, and use of commercial fertilizers such as urea, super phosphate of lime and insecticides such as DDT (dichloro diphenyl trichloroethane). There is every hope that chemistry will develop new drugs for controlling birth rate and hence to curb the very fast increasing world population. Chemists are busy in devising new adsorbents for checking harmful air pollution (due to increased industrialisation) and conditions for the growth of certain micro-organisms for destroying pollutants in water. Attempts are being made to utilise the nuclear energy and solar energy for meeting our energy requirements in near future, since reserves of coal and petroleum has been exhausting at a very fast rate. Attempts are also in progress to conquer the diseases of the heart and cancer (which are major killer of mankind these days).

Chemists in our country are trying hard to solve the various problems faced by the nation. Constant research is going on in National research laboratories, Institutes of technology, Universities and other research organisations.

QUESTIONS

(A) *Essay Type*

1. Does science provide absolute truth? Why or why not?
2. Should scientists be responsible for the ways in which society uses scientific discoveries?
3. List the five principal branches of chemistry and give the area covered by each branch.
4. With what is the science of chemistry concerned?
5. Trace the progression of a concept from hypothesis to theory to law.
6. Write a short essay on "chemistry in the service of humanity."
7. Discuss the terms law, theory and hypothesis. How are they inter related?



Atoms

2.1. INTRODUCTION

The nature of matter has been the subject of much speculation and study since the time of the early Greek philosophers. Ancient Indian philosopher, Kanada, had suggested that matter is ultimately composed by very small and indivisible particles called *parmanus*. Similarly, Democritus, a Greek philosopher, believed that matter is not continuous but is made up of tiny indivisible particles termed *atoms* (from the Greek word *atoms*, meaning uncut or indivisible). However, the ideas of these philosophers were not accepted universally due to lack of experimental evidence to support these.

As time passed, observations concerning the qualitative and quantitative behaviour of matter were recorded in the form of laws of chemical combinations. A brief review of these laws is given below :

1. **Law of conservation of mass.** This law was stated by Lavoiser in 1774. According to it *"matter is neither created nor destroyed in the course of a chemical reaction although it may change from one form to another."*

2. **Law of constant composition or definite proportions.** This law was first stated by Proust in 1799, and subsequently varified, mainly by Stas, in 1865. This law states that *"all pure samples of the same chemical compound contain the same elements combined together in the same proportion by weight"*. It means that pure specimens of a compound, no matter how, or where, or when or by whom they are made will always have identical compositions.

3. **Law of multiple proportions.** The law was first put forward by John Dalton in 1803. According this law *"when two elements A and B combine together to form more than one compound, the several weights of A which combine with a fixed weight of B are in a simple ratio"*.

4. **Law of reciprocal proportions** was first stated by Richter in 1792. This states that *"the weights of A, B and C, etc. which combine separately with some fixed weight of another element are the weights in which A, B, C, etc. will combine with each other, or simple multiples of them"*.

Based upon the information gathered in the forms of laws of chemical combinations, John Dalton, an English chemist—school master, proposed, in 1803, a concept concerning the inherent character of matter. In essence, Dalton's theory was this :

1. *All matter is composed of extremely tiny, discrete particles, called "atoms".*

2. *All atoms of the same chemical element have the same mass.*

3. *Atoms of different elements have different masses.*

4. *Atoms do not divide into smaller particles during chemical changes.*

5. *Compounds atoms (now called, molecules) are formed by the chemical combination of atoms in small, whole numbers.*

During most of the nineteenth century, the significance of this theory was paramount, because it permitted more rational predictions of undiscovered chemical phenomena and better explanations of the behaviour of matter. However, as more and more facts about matter came to light through later discoveries, Dalton's theory had to be reviewed and modified to explain the new observations.

2.2. MOLECULAR THEORY

In 1808, Gay-Lussac, gave the law of combining volumes which states that "*when gases react they do so in volumes which bear a simple ratio to each other and to the volume of any gaseous products, all volumes being measured under the same conditions of temperature and pressure*". Typical results, used by Gay-Lussac, are

(a) Oxygen	+	Hydrogen	→	Steam
1 Vol.		2 Vols.		2 Vols.
(b) Nitrogen	+	Hydrogen	→	Ammonia
1 Vol.		3 Vols.		2 Vols.
(c) Nitrogen	+	Oxygen	→	Nitric Oxide
1 Vol.		1 Vol.		2 Vols.

Atoms, according to Dalton, combined together in small, whole-number ratios, and gases, according to Gay-Lussac, combined, by volume, in small whole number ratios. It seemed more likely that there must be some relation between atoms and volumes of gases, and Dalton suggested that "*equal volumes of all gases, under similar conditions, contained the same number of atoms.*" Such a suggestion was not tenable, however, for it would lead to the view that atoms were divisible. For example, in the reaction between hydrogen and oxygen,

1 vol. of hydrogen + 1 vol. of chlorine → 2 vols. of hydrogen chloride

and, on Dalton's assumption that equal volumes of all gases contain in equal number of atoms.

1.8 | ESSENTIALS OF CHEMISTRY

∴	n atom of hydrogen	+	n atoms of chlorine	→	$2n$ compound atoms (molecules) of hydrogen chloride
or	1 atom of hydrogen	+	1 atom of chlorine	→	2 compound atoms (molecules) of hydrogen chloride
or	$\frac{1}{2}$ atom of hydrogen	+	$\frac{1}{2}$ atom of chlorine	→	1 compound atom (molecule) of hydrogen chloride

Thus, 1 compound atom of hydrogen chloride should have formed from half atom each of hydrogen and chlorine. But because atoms are indivisible this is absurd. Dalton reacted to this, by suggesting that Gay-Lussac's law was not true because it was based on inaccurate measurements.

The problem was, however, solved by a bold and imaginative suggestion made by Avogadro in 1811, and now known as "**Avogadro's hypothesis**". This states "*equal volumes of all gases, under similar conditions of temperature and pressure, contain equal number of molecules*" (not atoms, as supposed by Dalton).

The significance of this is that elements might exist as group of atoms (molecules) rather than as single atoms. In modern terms, the idea of the atomicity of an element (*i.e.*, the number of atoms in one molecule of an element) was born and indivisible atom was joined by another equally important particle, the molecule, which could be divided.

On the basis of Avogadro's hypothesis, Gay-Lussac's experimental results can be accounted for as follows.

1 volume of hydrogen	+	1 volume of chlorine	→	2 Volumes of hydrogen chloride.
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On applying Avogadro's hypothesis, we get

n molecules of hydrogen	+	n molecules of chlorine	→	$2n$ molecules of hydrogen chloride
or 1 molecule of hydrogen	+	1 molecule of chlorine	→	2 molecules of hydrogen chloride
or $\frac{1}{2}$ molecule of hydrogen	+	$\frac{1}{2}$ molecule of chlorine	→	1 molecule of hydrogen chloride.

Therefore, number of atoms in the molecule of hydrogen, chlorine and hydrogen chloride must be even. Or the above reaction can be expressed as :



where x and y must have whole-number values. The molecule of hydrogen, must, be H_2 or H_4 or H_6 , etc. That it is H_2 is supported by following evidences.

(i) The value of the ratio of the specific heats of hydrogen indicates that it is *diatomic*.

(ii) 1 volume of hydrogen is never known to produce more than 2 volumes of any gaseous products in any reaction. In other words, 1 molecule of hydrogen is never known to split up into more than 2 atoms. The atom of hydrogen is, therefore, half the molecule, so that the molecule is probably, H_2 .

(iii) Hydrogen chloride dissolves in water to form hydrochloric acid and this acid forms only one type of salts. This means that the acid is monobasic, and that its correct formula is probably HCl_x . If this is so, the value of x in equation (i) above is 1 and hydrogen is diatomic.

2.3. ATOMIC-MOLECULAR THEORY OF MATTER

As a result of about the last two centuries of experimentation and thought, the "atomic-molecular theory of matter" has come to be universally accepted. Accordingly :

(1) *All elements exist in the form of particles called 'atoms', each having a structure characteristics of the particular element.*

(2) *Atom is the smallest particle of an element which can enter into a chemical combination.* For example, one atom of carbon can combine with two atoms of oxygen to form one molecule of carbon dioxide.

(3) *An atom of an element may or may not be capable of independent existence.*

(4) *'Molecule' is defined as smallest particle of element or compound, capable of independent existence.*

(5) *The number of atoms in one molecule of an element is called the 'atomicity' of the element.* Thus, when the molecule of an element contain only one atom it is said to be "monoatomic". Examples of elements which are composed to monoatomic molecules are helium, neon and mercury. Hydrogen, oxygen, nitrogen, fluorine, chlorine, bromine and iodine consists of diatomic molecules (i.e., two atoms per molecule). Molecules of phosphorus and sulphur normally contain four and eight atoms, respectively.

(6) *The atom may be considered to be made up of a nucleus around which are found the electrons in certain definite groupings, depends upon the particular kind of atom.* The nucleus is made up of protons and neutrons, both of which are called 'nucleons'. The neutron has no charges ; whereas the proton has charge of plus one. Since the atom is electrically neutral, the number of electrons around the nucleus must be equal to the number of protons in the nucleus. The number of protons in the nucleus is the same for all the atoms of a given element. This number, called the atomic number, must be equal to the charge on the nucleus of the particular element and also equal to the number of electrons around the nucleus.

(7) *The chemical properties of a given element depend on the number and arrangement of the electrons.*

(8) Although the number of protons in the nucleus is always the name for a given element, the number of neutrons may be different because of existence of *isotopes*. For example, oxygen has

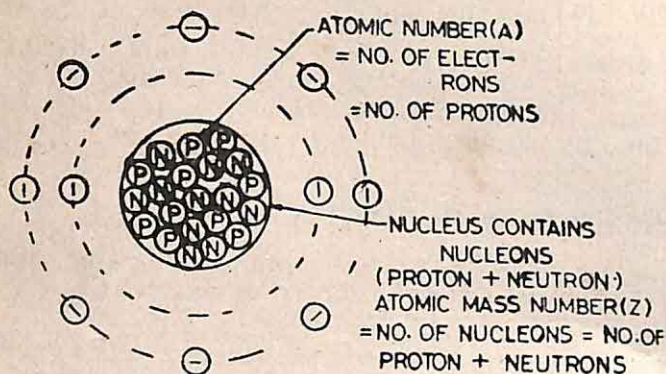


Fig. 2.1. Structure of an atom.

an atomic number of eight since it has eight protons in the nucleus. Oxygen as we find it in air, however, occurs in three different forms, one with eight, one with nine and one with ten neutrons associated with the protons. These three forms are the naturally occurring isotopes of oxygen ^{16}O , ^{17}O and ^{18}O . By definition, then, we may say that the *isotopes of an element are various forms of that element having identical chemical properties but differing in their actual masses*.

(9) It is not difficult to obtain the actual masses of atoms, but the values so obtained are too small that it would be inconvenient and cumbersome to employ them in chemical calculations. A more convenient method is to use the **atomic mass of an element**. This is the average mass of the atoms of the elements as they occur in nature relative to the mass of the most abundant isotope of carbon taken as 12.0000.

(10) The **atomic mass unit** (abbreviated as *amu*), by definition, represents one twelfth ($\frac{1}{12}$) of the mass of most abundant isotope of carbon atom (^{12}C).

(11) The **molecular mass** of a compound is the mass of a molecule of that compound compared to the mass of the most abundant isotope of carbon taken as 12.000.

(12) The number of grams of an element numerically equal to the molecular mass is termed as **gram molecular mass**. For example, the molecular mass of ammonia is 17.03 and 17.03 grams of ammonia is a gram-molecular mass.

2.4. THE MOLE CONCEPT

Chemical reactions take place between large number of particles, which may be *atoms*, *molecules* or *ions* (charged particles). Each of these particles has its own relative mass, but there is no general proportionality between amounts of each

substance and mass. The need for a basic independent unit for amount of substance was therefore put forward some years ago. The unit is **mole**, symbol n . The mole is the amount of substance which contains the same number of particles as there are atoms in 12 g (0.012 kg) of carbon-12. This number is Avogadro's constant, N_A , which has been determined as 6.023×10^{23} . The abbreviation for mole is *mol*.

It should be emphasized here that a mole is a practical unit of the amount of substance, as distinct from mass. The concept of the mole may be applied to molecules, atoms, ions, electrons, or

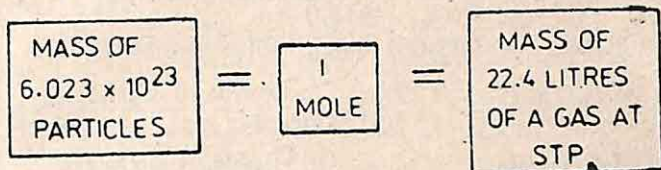


Fig. 2.2. Mole concept.

indeed protons; it is therefore essential always to specify the particles concerned. For example,

A mole of hydrogen molecules (H_2) has a mass of 2.016 g.

A mole of silver atoms has a mass of 107.868 g.

A mole of sulphate ions (SO_4^{2-}) has a mass of 96.06 g.

A mole of hydrogen atoms (H) has a mass of 1.008 g.

A mole of electrons (e^-) has a mass of 6.486×10^{-4} g.

A mole of carbon atom (^{12}C) has a mass of 12.000 g.

It may be pointed out here that in case of gases, it has been found that *the volume occupied by one mole of any gas at standard conditions of temperature and pressure (STP) is 22.4 litres*. This is taken as *molar volume of gases*.

SOLVED PROBLEMS ON MOLE CONCEPT

Example 2.1. How many atoms of oxygen are present in 0.5 mole of oxygen atoms?

Number of atoms

$$\begin{aligned}
 &= n \times N_A \\
 &= 0.5 \text{ mol.} \times 6.023 \times 10^{23} \text{ atom} \\
 &= 3.0115 \times 10^{23} \text{ atoms.}
 \end{aligned}$$

Example 2.2. How many moles of sulphur atom are there in 80 g of sulphur?

Moles of sulphur atoms

$$\begin{aligned}
 &= \frac{\text{Garms of S}}{\text{Atomic mass of S}} = \frac{80 \text{ g}}{32 \text{ g/mol}} \\
 &= 2.50 \text{ moles.}
 \end{aligned}$$

Example 2.3. How many moles of sulphur molecules are there in 80 g of sulphur, if the molecular formula of sulphur is S_8 ?

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1 mole of S_8 molecule has a mass of $8 \times 32 \text{ g} = 256 \text{ g}$.

$$\begin{aligned} \therefore \text{Mole of } S_8 &= \frac{\text{Grams of } S_8}{\text{Molecular mass of } S_8} = \frac{80.0 \text{ g}}{256 \text{ g/mol}} \\ &= 0.313 \text{ mol.} \end{aligned}$$

Example 2.4. How many moles are represented by 138 g of ethyl alcohol (C_2H_5OH) ?

The molecular mass of C_2H_5OH is calculated as follows ;

$$2C = 2 \times 12.0 = 24.0$$

$$6H = 6 \times 1.0 = 6.0$$

$$1O = 1 \times 16.0 = 16.0$$

$$\therefore \text{Molecular mass of } C_2H_5OH = 46.0$$

$$\therefore \text{Moles of } C_2H_5OH = \frac{\text{Grams of } C_2H_5OH}{\text{Molecular mass of } C_2H_5OH}$$

$$\begin{aligned} \therefore \text{Moles of } C_2H_5OH &= \frac{\text{Grams of } C_2H_5OH}{\text{Molecular mass of } C_2H_5OH} \\ &= \frac{138 \text{ g}}{46 \text{ g/mol}} \\ &= 3.0 \text{ moles.} \end{aligned}$$

Example 2.5. How many (a) grams of H_2S , (b) grams of H and S , (c) molecules of H_2S , (d) atoms of H and S are contained in 0.4 mole H_2S ?

$$\begin{aligned} \text{Molecular mass of } H_2S &= 2 \times \text{Atomic mass of H} \\ &\quad + \text{Atomic mass of S} \\ &= 2 \times 1.01 + 1 \times 32.06 \\ &= 34.08. \end{aligned}$$

$$\begin{aligned} (a) \text{ No. of grams of } H_2S &= \text{Number of moles} \times \text{Mass of mole} \\ &= 0.4 \text{ mol} \times 34.08 \text{ g/mol.} \\ &= 13.63 \text{ g.} \end{aligned}$$

$$(b) \text{ No. of grams of element} = \text{Atomic mass of element} \times \text{Number of moles of element} \times \text{Number of atoms in 1 molecule of element.}$$

$$\therefore \text{Grams of H} = 1.01 \times 0.4 \times 2 = 0.808 \text{ g.}$$

$$\text{Grams of S} = 32.06 \times 0.4 \times 1 = 2.86 \text{ g.}$$

$$(c) \text{ No. of molecules} = \text{Number of moles} \times \text{Number of molecules in 1 mole.}$$

$$= 0.4 \text{ mol} \times 6.023 \times 10^{23} \text{ molecules/mol}$$

$$(d) = 2.41 \times 10^{23} \text{ molecules.}$$

$$\begin{aligned} \text{No. of atoms of element} &= \text{No. of molecules} \times \text{No. of atoms of element/molecule} \end{aligned}$$

$$\therefore \begin{aligned} \text{No. of atoms of H} &= 2.41 \times 10^{23} \times 2 = 4.82 \times 10^{23} \text{ atoms.} \\ \text{No. of atoms of S} &= 2.41 \times 10^{23} \times 1 = 2.41 \times 10^{23} \text{ atoms.} \end{aligned}$$

Example 2.6. How many (a) moles of P atoms, (b) moles of P_4 molecules, (c) molecules are contained in 92.91 g phosphorus ?

(a) 1 mole of P atoms has a mass of 30.974 g.

$$\therefore \text{No. of moles of P atoms} = \frac{92.91 \text{ g.}}{30.97 \text{ g/mole}} = 3.00 \text{ moles P.}$$

(b) 1 mole P_4 molecules has a mass of $4 \times 30.974 \text{ g} (=123.90 \text{ g})$

$$\therefore \text{No. of moles present} = \frac{92.91 \text{ g}}{123.90 \text{ g/mole}} = 0.75 \text{ mole } P_4.$$

$$\begin{aligned} \text{(c) Molecules of } P_4 &= 0.75 \text{ mol.} \times 6.023 \times 10^{23} \\ &\quad \text{molecules mol.}^{-1} \\ &= 4.517 \times 10^{23} \text{ molecules.} \end{aligned}$$

Example 2.7. Calculate the number of molecules in 11.2 8 litres of hydrogen gas at STP.

$$22.4 \text{ litres at STP} = 1 \text{ mol}$$

$$\therefore \begin{aligned} 11.2 \text{ ,, ,, ,,} &= \frac{11.2}{22.4} \\ &= 0.5 \text{ mol } H_2. \end{aligned}$$

$$\begin{aligned} \therefore \text{No. of molecules of } H_2 &= \text{No. of mol.} \times \text{No. of molecules mol.}^{-1} \\ &= 0.5 \times 6.023 \times 10^{23} \text{ molecules} \\ &= 3.0115 \times 10^{23} \text{ molecules.} \end{aligned}$$

Example 2.8. Which of the following weights most ? (i) 1 mole of Na_2CO_3 , (ii) 10 grams atoms of helium, (iii) 22.4 litres of CO_2 at STP, (iv) 6.023×10^{24} atoms of hydrogen ? (Atomic masses of $Na=23$, $C=12$, $O=16$, $H=1$)

$$\begin{aligned} \text{(i) 1 mole of } Na_2CO_3 \text{ has a mass} &= 2 \times 23 + 1 \times 12 + 3 \times 16 \text{ g} \\ &= 106 \text{ g.} \end{aligned}$$

$$\text{(ii) 1 gram-atom of helium has a mass} = 4 \text{ g.}$$

$$\therefore \begin{aligned} 10 \text{ ,, ,, ,, ,,} &= 4 \times 10 \text{ g} \\ &= 40 \text{ g.} \end{aligned}$$

$$\begin{aligned} \text{(iii) 22.4 litres of } CO_2 \text{ at STP} &= 1 \text{ mol.} \\ &= (1 \times 12 + 2 \times 16) \text{ g} \\ &= 44 \text{ g.} \end{aligned}$$

$$\begin{aligned} \text{(iv) } 6.023 \times 10^{23} \text{ atoms of hydrogen} &= 1 \text{ g.} \\ \therefore 6.023 \times 10^{24} \text{ atoms of hydrogen} &= \frac{6.023 \times 10^{24}}{6.023 \times 10^{23}} \text{ g} \\ &= 10 \text{ g.} \end{aligned}$$

Hence, 1 mole of Na_2CO_3 weights most.

2.5. RUTHERFORD'S MODEL OF ATOM

To explain the various observations, during studying the scattering of alpha-particles by thin gold foil, Rutherford (1911) proposed the following *atomic model*.

(1) *A neutral atom consists of a very tiny positively charged nucleus (of diameter about 10^{-13} cm) which contains practically the whole mass of the atom.*

(2) *The nucleus is surrounded by electron and atom is largely empty.*

(3) *The number of electrons outside the nucleus equals the number of units of positive charge in the nucleus.*

(4) *The electrons are not stationary, but are revolving around the nucleus in closed orbits. Their centrifugal force balance the force of attraction and keeps them in their path.*

2.6. DRAWBACK OF RUTHERFORD'S MODEL

According to Rutherford's atomic model, the electrons are orbiting around the nucleus and hence the direction of their velocity is constantly changing, i.e., electrons are accelerating. But this acceleration will cause the electron to emit or radiate energy and consequently the electron will have lesser and lesser energy and will get closer and closer to the nucleus until at last it spirals into the nucleus (see Fig. 2.3).

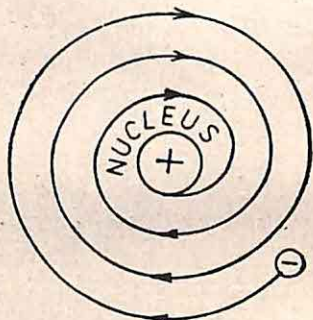


Fig. 2.3

2.7. NATURE OF LIGHT AND ELECTRO-MAGNETIC SPECTRUM

Light has played a key-role in the study of atomic spectra, so, we could like to consider some salient aspects of the nature of light. According to Newton's **Corpuscular theory**, *light is propagated as a stream of particles, called corpuscles*. This theory could justify the phenomena of reflection and refraction of light, but failed to explain the phenomena of diffraction, interference, etc. In 1856, Clerk Maxwell suggested that light waves are associated with both electric and magnetic fields, i.e., light may be described as electromagnetic waves or radiations. There are three characteristic properties associated with any kind of wave e.g.,

(i) **Wave length** is the distance between the two neighbouring crests or troughs of a wave (see Fig. 2.4). It is generally symbolised by the Greek letter lambda, λ and is generally expressed in Angstrom units ($\text{\AA} = 1 \times 10^{-8}$ cm.). The colour of a beam of visible light is determined by its wave length.

(ii) **Frequency** is the number of waves per second. It is denoted by the Greek letter nu, ν . Its unit is cycle per second (cps) or Hertz (Hz).

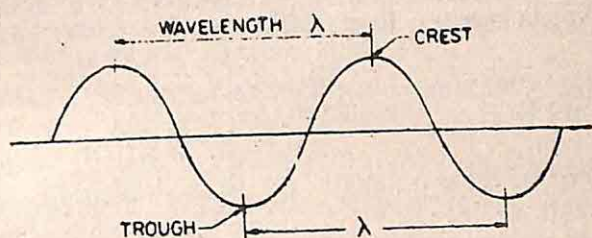


Fig 2.4. Wave motion.

(iii) **Velocity** is the distance travelled by the wave in one second. It is denoted by the letter c and is equal to the product of wavelength and frequency, i.e.,

$$c = \lambda \times \nu$$

or

$$\nu = \frac{c}{\lambda}$$

The velocity of an electromagnetic radiation is found to be constant (i.e., $3 \times 10^8 \text{ m s}^{-1}$ or $3 \times 10^{10} \text{ cm s}^{-1}$) and independent of the medium in which it travels because the electromagnetic wave do not require any medium for propagation. Thus, all electromagnetic radiations travel with the same velocity, but may differ in their wavelength or frequency.

Visible light (i.e., light which our eyes can detect) consists of electromagnetic radiations whose wavelengths, range between 3700 \AA (violet) to nearly $7,500 \text{ \AA}$ (red). Visible light represents only a small part of all radiation, and a more complete representation of the possible types of radiations is given in Fig. 2.5.

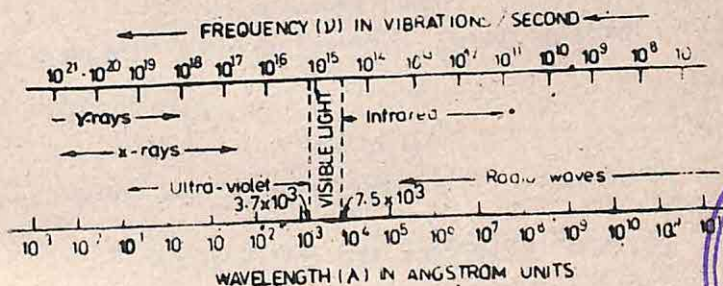


Fig. 2.5. The electromagnetic spectrum.

2.8. QUANTUM THEORY

Max Planck (1900) proposed a theory according to which :

(1) The energy of a body can only change by some definite whole number multiple of a unit of energy known as the 'quantum'.

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This means that the energy of a body can increase or decrease by, 1, 2, 3, 4, n quanta, but never by $1\frac{1}{2}$, $2\frac{1}{3}$, 106.3, etc. quanta.

(2) *The value of quantum is not fixed, but is related to the frequency of radiation which, by its emission or absorption, causes the change in energy.* This relationship is expressed as :

$$\begin{array}{lcl} E & = & h \times \nu \\ \text{(Value of quantum)} & & \text{(Planck's constant)} \quad \text{(Frequency of radiation)} \\ \text{in kJ} & = & 3.99 \times 10^{-15} \text{ kJ sec. mol}^{-1} \end{array}$$

or in terms of the wavelength (λ) of the radiation and the velocity of light (c), as :

$$E = \frac{hc}{\lambda}$$

Example 2.9. *What is the frequency of a radiation of visible light having a wavelength of 7500 Å?*

We know : $\nu = \frac{c}{\lambda}$

Here $c = 3 \times 10^{10} \text{ cm sec}^{-1}$ $\lambda = 7500 \text{ Å} \times 10^{-8} \text{ cm}$.

$$\begin{aligned} \therefore \text{Frequency} &= \frac{3 \times 10^{10}}{7500 \times 10^{-8}} = 4 \times 10^{14} \text{ cps.} \\ &= 4 \times 10^{14} \text{ Hz.} \end{aligned}$$

Example 2.10. *Which has the higher energy, a photon of red light with a wavelength of 7500 Å or a photon of violet light with a wavelength of 3750 Å? ($h = 3.99 \times 10^{-13} \text{ kJ sec mol}^{-1}$.)*

We know : $E = h\nu$

\therefore Energy possessed by red light photon

$$\begin{aligned} &= \frac{3.99 \times 10^{-13} \times 3 \times 10^{10} \text{ kJ mol}^{-1}}{7500 \times 10^{-8}} \\ &= 160.5 \text{ kJ mol}^{-1}. \end{aligned}$$

Similarly, energy possessed by violet light photon

$$\begin{aligned} &= \frac{3.99 \times 10^{-13} \times 3 \times 10^{10} \text{ kJ mol}^{-1}}{3750 \times 10^{-8}} \\ &= 321 \text{ kJ mol}^{-1}. \end{aligned}$$

Hence, violet light photon with shorter wavelength is more energetic than red light photon.

2.9. ATOMIC SPECTRA OF HYDROGEN

If the light from an electric filament lamp is examined by a spectroscope, it is found to consist of all visible wavelengths, i.e., it gives a continuous spectrum. The light from a mercury vapour lamp, however, is made up of a limited number of wavelengths, and its spectrum, known as a line spectrum, consists of a series of sharply defined lines each corresponding to a definite wavelength. Excited vapour of every element similarly gives rise to a line spectrum. Thus, line spectra are characteristic of atoms.

Hydrogen spectrum consists of lines corresponding to widely different frequencies. However, over a period of time, starting in 1885, it was found that many of the numerous lines could be fitted into series. These series known after their discoverers as the Balmer (1885), Paschen (1896), Lyman (1915) and Bracket (1922) series, can be expressed in one overall formula :

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n^2} - \frac{1}{m^2} \right)$$

where λ is the wavelength, R_H a constant, known as Rydberg's constant, and n and m have integral values as given below :

Series	n	m
Lyman	1	2,3,4, etc.
Balmer	2	3,4,5, etc.
Paschen	3	4,5,6, etc.
Bracket	4	5,6,7, etc.
Pfund	5	6,7,8, etc.

2.10. BOHR'S INTERPRETATION OF SPECTRAL LINES

In order to overcome the drawback against Rutherford's atomic model, Neils Bohr (1913) used the quantum theory to explain why electrons keep on revolving round the nucleus without losing energy. He made following **postulates** :

(1) *An atom consists of a massive positively charged central core (called, nucleus) with electrons revolving around it in circular path called, orbits. The nucleus itself is at rest.*

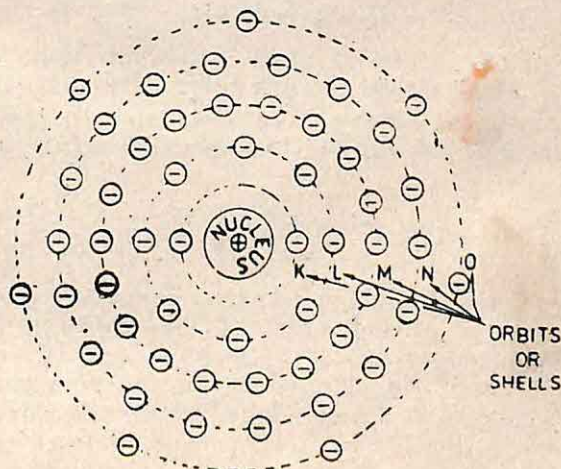


Fig 2.6. Representation of Bohr's energy level.

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(2) To keep the electrons revolving in orbit and to prevent them from spiralling in towards the nucleus, the inward centripetal force required is provided by inward electrostatic attraction between the electrons and the nucleus.

(3) *The electrons cannot move in any size orbit, i.e., can move in just certain definite or discreet and permitted orbit (or stationary orbit) without loss (or radiation) of energy.*

(4) The size of the allowed or stationary orbit or shell is such that *the angular momentum of the electron is an integral multiple of $h/2\pi$, i.e.,*

$$\text{Angular momentum} = nh/2\pi$$

where h = Planck's constant and n is called the Principal quantum number, which can take only whole number values 1, 2, 3, 4, 5, etc. The various orbits or shells are designated by letters K, L, M, N , etc. for 1st, 2nd, 3rd, 4th, etc. orbit starting from the nucleus respectively (see fig. 2.6). More the orbit (or shell or level) is away from the nucleus the greater is the energy associated with it.

(5) *As long as the electron remains in a particular orbit or shell it neither emits nor absorbs energy.*

(6) *Energy is emitted or absorbed by an atom only when an electron moves or jumps from one level to another.*

(7) *The emission of radiant energy is caused by the movement of an electron from one stationary state to another of lower energy. Conversely, absorption of energy takes place when an electron moves into a stationary states of higher energy.* Thus, if the energy of one stationary state is given as E_1 and that of the next stationary state with lower values as E_2 , an electron passing from the first to the second would cause an energy change of $E_1 - E_2$, and an emission of radiation of frequency is given by :

$$\Delta E = E_1 - E_2 = h\nu = hc/\lambda$$

Based on above theory of atomic structure, Bohr derived following general mathematical expression for calculating the wave number $\bar{\nu}$ (i.e., number of waves per centimeter and frequency (ν) radiation when the lone electron of hydrogen moves from one orbit to another.

$$\frac{\nu}{c} = \bar{\nu} = 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1}$$

According to Bohr, the single electron keeps on rotating in the energy level 1 (i.e., ground state) of the hydrogen atom. On exposure to some external source of energy (such as electrical discharge or radiation of suitable wave-length) the atom gets excited i.e., the electron jumps to a higher energy level by absorbing energy. When the excited electron returns to lower energy level, it emits a quanta of energy in the form of light of certain frequency and thus gives rise to line spectrum.

Lyman series of spectral lines are observed when $n_1=1$, and $n_2=2, 3, 4$, etc. **Balmer series** is obtained when electron jumps from the energy level 3rd, 4th, 5th, etc. to the second energy level, i.e., when $n_1=2$ and $n_2=2, 3, 4$, etc. Similarly, **Paschen, Brackett** and **Pfund** series of spectral lines are obtained (see Fig. 2.7). It may be pointed here that the frequency of the spectral lines observed in hydrogen have been found to be excellently in accord with those predicted by Bohr's theory.

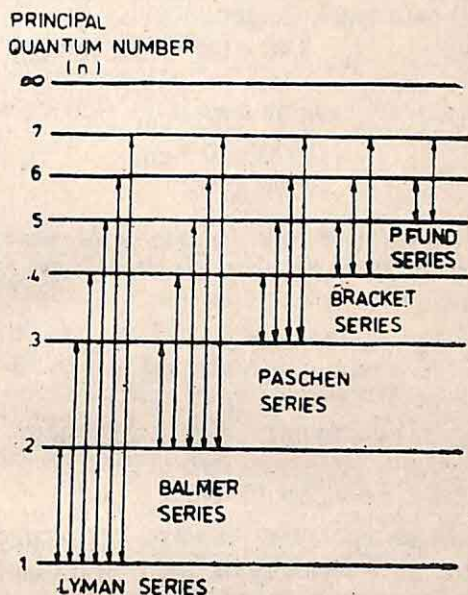


Fig. 2.7. Illustration of the energy changes which an electron can undergo in moving from one energy level to another in hydrogen atom. The integers on the left represent the stationary state numbers (or Principal quantum numbers).

Example 2.11. The energy difference between two electronic states of hydrogen atom is $214.68 \text{ kJ mol}^{-1}$, calculate the frequency of light emitted when an electron drops from the higher to the lower state. Planck's constant, $h=3.979 \times 10^{-13} \text{ kJ sec mol}^{-1}$.

We know that the energy difference of the electronic states ($\Delta E = E_1 - E_2$) is related to the frequency (ν) of radiation as :

$$\Delta E = E_1 - E_2 = h\nu$$

$$\text{or} \quad \nu = \frac{\Delta E}{h}$$

Substituting $h=3.979 \times 10^{-13} \text{ kJ sec. mol}^{-1}$, $\Delta E=214.68 \text{ kJ mol}^{-1}$, we get.

Frequency,

$$\begin{aligned}
 &= \frac{214.68 \text{ kJ mol}^{-1}}{3.979 \times 10^{-13} \text{ kJ sec mol}^{-1}} \\
 &= 5.39 \times 10^{14} \text{ sec}^{-1}.
 \end{aligned}$$

Example 2.12. The energy difference between two electronic states of hydrogen atom is $245.9 \text{ kJ mol}^{-1}$. Calculate the wavelength of light emitted when an electron drops from the higher to the lower state (Planck's constant $h = 3.98 \times 10^{-13} \text{ kJ sec mol}^{-1}$)

We know : $\Delta E = h\nu = \frac{hc}{\lambda}$.

$\therefore \lambda = \frac{hc}{\Delta E}$

Substituting here $h = 3.98 \times 10^{-13} \text{ kJ sec mol}^{-1}$; $\Delta E = 245.9 \text{ kJ mol}^{-1}$; $c = 3 \times 10^{10} \text{ cm sec}^{-1}$, we get

$$\begin{aligned}\lambda &= \frac{3.98 \times 10^{-13} \times 3 \times 10^{10} \text{ cm}}{245.9} \\ &= 4.97 \times 10^{-5} \text{ cm} \\ &= 4970 \times 10^{-8} \text{ cm} \\ &= 4270 \text{ \AA}.\end{aligned}$$

Example 2.13. Calculate the frequency of the line in the emission spectrum of hydrogen when its electron drops from third to first energy level.

We know : $= 109,677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$

Here $n_1 = 1$; $n_2 = 3$

$\therefore \nu = 109,677 \left(\frac{1}{4} - \frac{1}{9} \right) \text{ cm}^{-1}$

$= 9.75 \times 10^4 \text{ cm}^{-1}$

= Number of waves per second

= Velocity of light in cm sec^{-1}
 \times Number of waves per cm

$= 3 \times 10^{10} \text{ cm sec}^{-1} \times 9.75 \times 10^4 \text{ cm}^{-1}$

$= 2.925 \times 10^{15} \text{ sec}^{-1}$.

2.11. DEFECTS OF BOHR'S MODEL

The Bohr's model although is the most important guide-post to the further studies of atomic phenomenon, has limited validity and it suffers from the following serious defects.

(1) Attempts to apply Bohr's theory to other elements (i.e., with more than one electron) were moderately successful and that too in a few cases. Hence, the Bohr's model is not a general solution to the problem of atomic structure.

(2) Even with hydrogen atom, Bohr's theory could not provide finer details of spectra. Sommerfeld found that in the hydrogen spectrum each line, of a series, consists of several closely spaced components, called the multiplicity structure.

(3) A complete analysis should not only reveal the frequency of the emitted light, but also the relative intensities of the spectral lines.

2.12. WAVE NATURE OF MATTER—DE BROGLIE'S EQUATION

In 1924 Louis de Broglie, a French theoretical physicist, reasoned that

- (1) *nature is strikingly symmetrical in many ways,*
- (2) *our observable universe is composed entirely of light and matter, and*
- (3) *if light has a dual wave-particle nature, perhaps matter also. In other words, he said, "A wave can be a particle, and a particle can be a wave".*

Based on this idea he predicted that the wave-length, corresponding to a particle with mass m and velocity v is given by the relationship.

$$\lambda = \frac{h}{mv}$$

The de Broglie idea of dual nature of matter was tested experimentally by C.J. Davission and L.H. Germer (1927) in which they showed that electron could be diffracted like a wave.

Example 2.14. Calculate the de Broglie's wave-length associated with an electron moving at a velocity of $6 \times 10^8 \text{ cm sec}^{-1}$ (Mass of an electron = $9.1 \times 10^{-28} \text{ g}$; Planck's constant, $h = 6.625 \times 10^{-27} \text{ erg-sec.}$)

We know de Broglie's wave-length,

$$\begin{aligned} \lambda &= h/mv \\ &= \frac{6.625 \times 10^{-27} \text{ erg sec}}{9.1 \times 10^{-28} \times 6 \times 10^8 \text{ cm sec}^{-1}} \\ &= 1.21 \times 10^8 \text{ cm} = 1.21 \text{ \AA}. \end{aligned}$$

2.13. HEISENBERG'S UNCERTAINTY PRINCIPLE

Prior to 1927, it has been thought that if mass, position, velocity, energy, etc. were known about a particle, the future activity of the particle could be predicted accurately by using Newton's law of motion. However, in 1927, Heisenbergs stated that "it is impossible to determine both position and momentum of a body simultaneously with perfect accuracy". Thus, if an experiment is designed to measure one of them exactly, the other will become uncertain and vice versa. This is because any measurement of a system disturbs the system, but the extent of the disturbance is indeterminate. In measuring mass, position, etc. of a particle, the particle is jolted and consequently has a different measured mass, position, etc. Because the disturbance is indeterminate, we cannot work backwards and take this disturbance into account in order to find the original mass, position, etc. This is true regardless of the delicacy with which the measurement is carried out.

An experiment can measure both position and momentum only within certain limits of accuracy. These limits are specified

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by the **Uncertainty or Indeterminacy Principle** (due to Heisenbergs) according to which—*“Given an object, the error in position of the object (no matter how large or how small) multiplied by the error in momentum of the object (no matter how large or how small) must be greater than or equal to Planck’s constant.”* Or mathematically.

$$\text{Error in position} \times \text{Error in momentum} \geq h$$

The uncertainty principle shows us why it is possible for light and matter to have a dual, wave-particle, nature. It is because these two views (obviously opposite to each other) can never be brought face to face in the same experimental situation. If we devise an experiment that forces the electron to reveal its particle character strongly, its wave character will always be inherently fuzzy. On the other hand, if we modify the experiment to bring out the wave character more strongly, its particle character will necessarily become fuzzy. Thus, the dual character of matter and light is like coins that can display either faces at one time but not both simultaneously. But to obtain the complete picture of any event we require both the wave and particle properties of the matter but it is impossible to design an experiment—to reveal both of them at the same time.

2.14. QUANTUM NUMBERS

An electron in an atom has some ‘location’ relative to the nucleus and is associated with some ‘energy’. These properties taken together describe the *state of the electron* in the atom. Different possible states available to an electron are determined by the laws of quantum mechanics. *In order to identify these states, numbers called quantum numbers are used.* Thus, quantum numbers specify the location and the energy of an electron.

The state of an electron can be described by a set of four quantum numbers.

(1) **Principal quantum number (n)** indicates the average distance from the nucleus and its average energy. It represents the shell number of orbit. This quantum number may have any integral values from unity, i.e., 1, 2, 3, 4, etc. With the increase in the value of n , the distance from the nucleus increases and its energy becomes higher and higher. Alternative letters K, L, M, N, O , etc., are used for first ($n=1$), second ($n=2$), third ($n=3$), fourth ($n=4$), fifth ($n=5$), etc., orbit or shell number.

(2) **Azimuthal or orbital quantum number (l)** determines the ellipticity of the orbit (or amount of rotational motion). It represents the various sub-shells within a shell. l may have integral values from 0 to $n-1$. For example :

n value	1	2	3	4
l value	0	0,1	0,1,2	0,1,2,3.

In other words, total number of values of l is equal to n . The

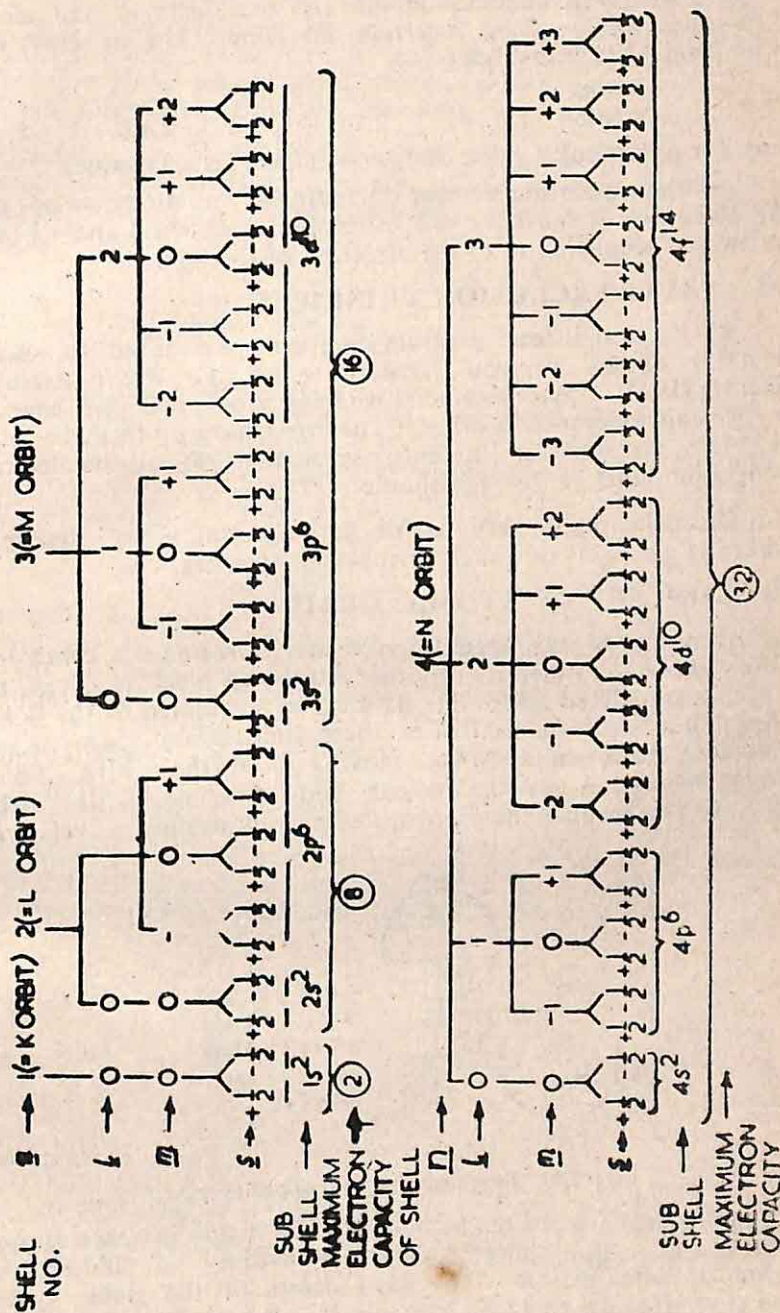


Fig. 2.8. Use of Pauli exclusion principle.

sub-shells with $l=0, 1, 2, 3$ are usually designated by letters s, p, d, f respectively.

(3) **Magnetic quantum number (m)** represents of the amount of rotational motion along a certain direction. The m may have value from $-l$ to 0 to $+l$, e.g.,

l value.	1	2	3
$m \times$ value	1, 0, -1	2, 1, 0, -1, -2	3, 2, 1, 0, -1, -2, -3

Thus, for a particular value of l , m will have $(2l+1)$ values.

(4) **Spin quantum number (s)** indicates the direction of spinning elec. \therefore It can have two values $+\frac{1}{2}$ (clock-wise) and $-\frac{1}{2}$ (anti-clockwise,) according to the direction of the spin.

2.15. PAULI EXCLUSION PRINCIPLE

We know that four quantum numbers are required to specify the states of an electron. According to the *Pauli exclusion principle* (1925) "No two electrons in the same atom can have all the four quantum numbers alike. They may have up to three alike but at least one must be different." In other words, all the electrons in any atom must be distinguishable.

This principle is very useful in determining the maximum number of electrons in a shell or sub-shell (see Fig. 2.8).

2.16. CONCEPT OF ATOMIC ORBITAL

According to **wave-mechanical theory**, electron is a completely mobile cloud of negativity. In other words, an electron does not have a well-defined path of its own as postulated by the Bohr's theory. Thus, electrons partrol in three-dimensional space around the nucleus much similar to bees moving about their hive. Sometimes an electron is near the nucleus and sometimes it is farther away. In this manner the electrons effectively occupy a relatively

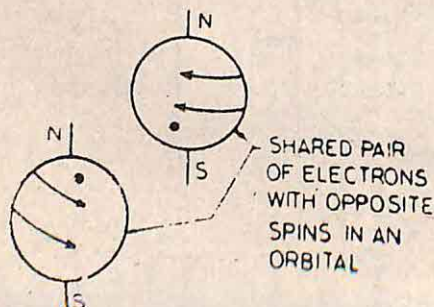


Fig. 2.9. Two electrons with opposite spins.

vast empty space around the nucleus. "The region in space around the nucleus in which there is high probability of finding the electron" is called **orbital**. The fixed orbits of the Bohr theory of the atom are now replaced by orbitals. It may be pointed out that the maximum capacity of an orbital is two electrons, that too if they are of opposite spins (see Fig. 2.9).

In order to get a physical picture, orbitals may be considered to have a 'size', a 'shape' and an 'orientation.' The *principal quantum number* (n) indicates the size. The higher the value of n , larger is the size of the orbital. The *azimuthal quantum number* (l) gives the shape of the orbital; while the *magnetic quantum number* (m) gives the orientation of the electron wave.

s-Orbitals. From wave-mechanical calculations the first (or K) shell can have $l^2=1$ orbital only. For $n=1$, l and m can have only one value (i.e., 0 each), therefore s-orbital can have only

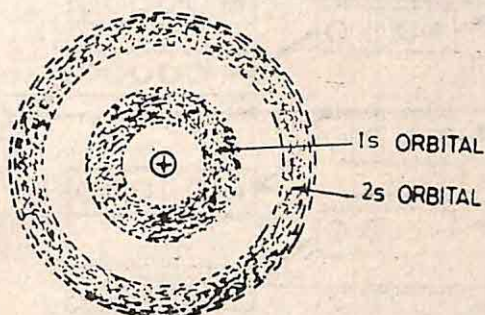


Fig. 2.10. 1s and 2s atomic orbitals.

one possible orientation, i.e., *spherical*. The second (or L) shell is made up of $2^2=4$ orbitals, which are of two types, i.e., 2s and 2p. The 2s-orbital is also spherical like the 1s-orbital, but having more sepacious concentric sphere. The 1s-and 2s-orbitals are separated by a region of zero electron density.

p-Orbitals have three possible orientation mutually at right angles in three-dimensional space around the nucleus. The p-orbitals are somewhat "dumb-bell" shaped as shown below :

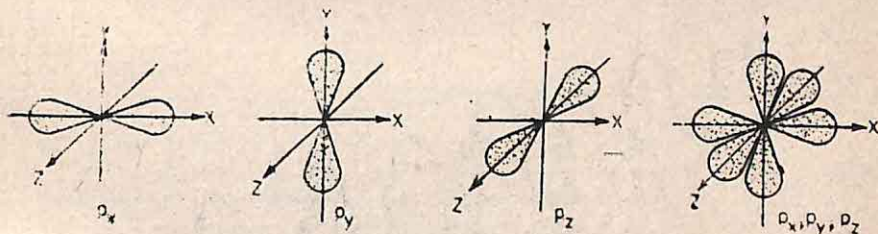


Fig. 2.11. p-atomic orbitals.

2.17. ORDER OF OCCUPATION OF ORBITALS BY ELECTRONS

As we pass from hydrogen atom (containing 1 electron in 1s orbital in its ground state) it is convenient to imagine that the next higher atom has essentially the same inner structure as the

preceding one and that one electron is added every time to the previous structure. Filling of the different orbitals by electrons proceeds in accordance with the following rules, collectively called as **Aufbau-Principle** (German : *aufbau*=building up.)

(1) *The orbitals are filled in the order of increasing energy, i.e., an orbital with lower energy is filled up first than another orbital of higher energy.* An approximate indication of the relative energies for various orbitals is given in Fig. 2.12.

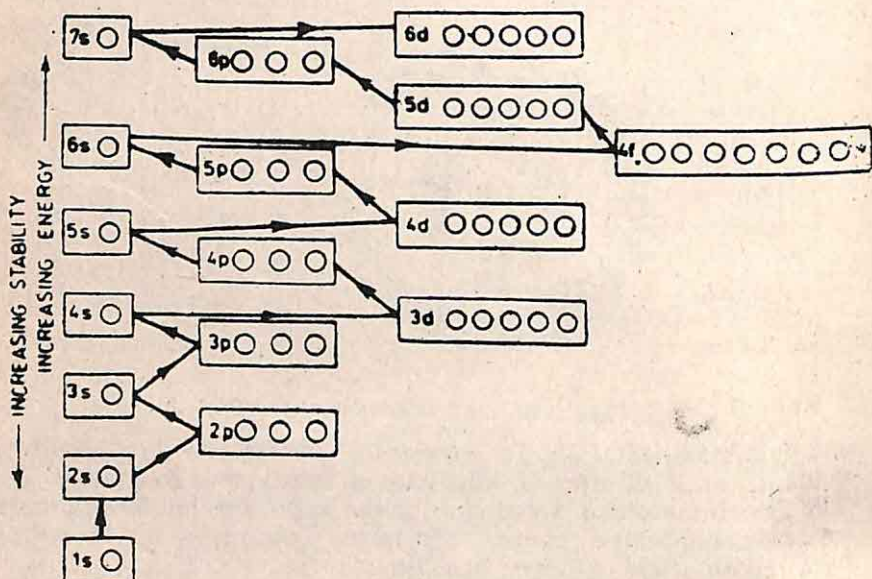


Fig. 2.12. Energy level diagram of orbitals in a many-electrons atom with approximate order in which they are filled.

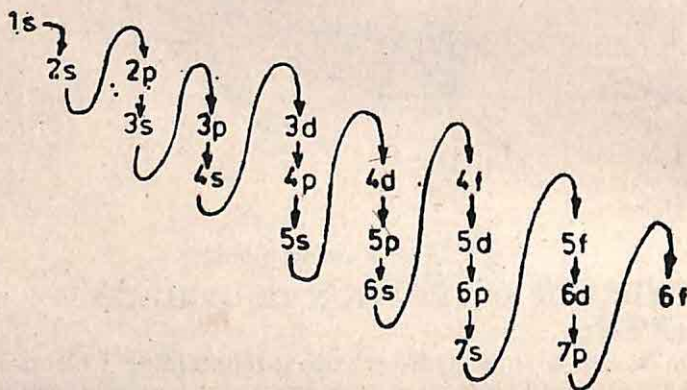


Fig. 2.13. Easy method of remembering the order of filling of orbitals.

Note. An exception to above order occurs where a single $5d$ -electron is added before $4f$ -orbital is occupied. However, the next 14 electrons enter the $4f$ -orbitals before any more electron enters the $5d$ -orbitals. This is because energies of $4f$ - and $5d$ -orbitals are very close to each other. Similarly, one or more electrons enter the $6d$ -orbitals before any electron occupies the $5f$ -orbitals.

(2) *The new electron enters that orbital where $(n+l)$ has minimum value; and if $(n+l)$ is same in two or more cases, the new electron will enter where n is minimum.* For example, we want to know whether a new electron will enter $2p$ - or $3s$ -orbital. The value of $n+l$ is $2+1=3$ for $2p$ -orbital and $3+0=3$ for $3s$ -orbital, i.e. 3 in each case. However, n is lower in case of $2p$ -orbital. Consequently, the new electron will enter the $2p$ -orbital and not $3s$ -orbital.

(3) *Electrons in any sub-shell (s, p, d , or f) occupy the orbitals singly to start with and have parallel spins before pairing in any orbital occurs.* This is separately known as **Hund's Rule of Maximum Multiplicity**. For example, if there are three electrons in p -orbitals in an atom, the arrangement p_x^1, p_y^1, p_z^1 and not p_x^2, p_y^1, p_z^0 . The application of Hund's rule is illustrated in Figure 2.14.

	1s	2s	2p _x	2p _y	2p _z
1H	↓				
2He	↑↓				
3Li	↑↓	↓			
4Be	↑↓	↑↓			
5B	↑↓	↑↓	↓		
6C	↑↓	↑↓	↓	↓	
7N	↑↓	↑↓	↓	↓	↓
8O	↑↓	↑↓	↑↓	↓	↓
9F	↑↓	↑↓	↑↓	↑↓	↓
10Ne	↑↓	↑↓	↑↓	↑↓	↑↓

Fig. 2.14. Illustration of application of Hund's Rule.

will be p_x^1, p_y^1, p_z^1 and not p_x^2, p_y^1, p_z^0 . The application of Hund's rule is illustrated in Figure 2.14.

(4) *Electrons tend to enter those sub-shells, which thereby get either completely filled or just-half-filled.*

(5) *The maximum capacity of each orbital is two electrons with spins of $+\frac{1}{2}$ and $-\frac{1}{2}$.*

QUESTIONS

(A) Essay Type :

1. Explain clearly the terms 'mole' and 'Avogadro number'. Define atomic mass and molecular mass on the basis of mole concept.
2. Write an essay on Dalton's atomic theory.
3. Write a note on molecular theory.
4. State briefly Dalton's atomic theory. In what respects has it been modified by modern researches?
5. Give the essential features of Bohr's model of the atom.
6. How does Bohr atomic theory interpret the line spectrum of hydrogen? What are the limitations of this theory?
7. Explain the terms frequency and wavelength. How are they related to each other?

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8. Write a short note on "quantum numbers".
9. What is Pauli exclusion principle? How does it permit us to construct model for the electronic configuration of atoms?
10. Write short notes on :
 - (a) Atomic orbitals,
 - (b) Particle and wave nature of the electron,
 - (c) Pauli's exclusion principle.
 - (d) Hund's rule of maximum multiplicity,
 - (e) Aufbau principle,
 - (f) Heisenberg's uncertainty principle.
11. What is an atomic orbital? Describe the shapes of s and p-orbitals.
12. What do you understand by the term dual character of matter? State de Broglie's equation.
13. Discuss briefly "quantum theory" of radiation.
14. Write an essay describing the modern views about the structure of atom.
15. Arrange the following in order of increasing frequencies : infrared radiations, visible light, gamma radiations, radio waves, ultraviolet radiations.
16. Which has the higher energy, a photon of red light with wave-length of 7,200 Å or a photon of violet light with a wave length of 4,000 Å?
17. Name the elements that correspond to each of the following configurations :
 - (a) $1s^2, 2s^2, 2p^2$.
 - (b) $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$.
 - (c) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$.
18. Arrange the following orbitals in order of increasing energy.
 $1s, 2s, 3s, 4s, 2p, 3p, 4p, 3d, 4d$.
19. An atom has the electronic configuration $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$. What is its atomic number?
20. Write the electronic configuration of atoms having atomic number 8, 11, 17, 19 and 20.
21. What is the maximum number of electrons in s, p, d, and f-orbitals of an atom?
22. Which of the following do and which do not make sense? Give reasons in support of your answer.
 $1p^1, 3s^2, 3p^1, 2s^3, 2d^3, 3f^8$.

(B) Objective Type :

Point out the correct statement in each of the following :

23. 6.023×10^{22} atoms of carbon is equal to
 - (a) 5 gram-atom of carbon,
 - (b) 1 mole of carbon,
 - (c) 0.1 gram-atom of carbon.
24. Mass of 2.24 litre of oxygen at STP is
 - (a) 32 g ; (b) 3.2 g ; (c) 16 g ; (d) 1.6 g.
25. The nucleus of an atom contains :
 - (a) Protons and electrons,
 - (b) Neutrons and electrons,
 - (c) Neutrons, electrons and protons,
 - (d) Neutrons and protons.

26. 1 gram atomic mass of any metal contains :
- | | |
|---|------------------------------------|
| (i) 1 atom, | (ii) 6.023×10^{24} atom, |
| (iii) 6.023×10^{23} molecules, | (iv) 6.023×10^{22} atoms, |
| (v) 6.023×10^{23} atoms, | (vi) 6.023×10^{23} ions. |
27. de Braglie equations is :
- | | |
|----------------------------------|-----------------------------------|
| (i) $h = \frac{\lambda}{mv}$; | (ii) $\lambda = \frac{h}{mv^2}$; |
| (iii) $\lambda = \frac{h}{mv}$; | (iv) $m = \frac{v}{\lambda h}$. |
28. Two electrons can have the same values of n, l, m but different values for s .
- (a) True, (b) False, (c) Don't know.
29. The electrons moving in fixed circular orbits are associated with a definite amount of energy.
- (a) True, (b) False, (c) Don't know.
30. With increasing value of n , the energy of orbits :
- (i) Decreases, (ii) Remain same, (iii) Increases.
31. The electron behaves as :
- (i) a particle, (ii) a wave, (iii) a wave and particle both.
32. The shape of p -orbit is :
- (a) Circular, (b) Dumb-bell, (c) Elliptical.
33. Three electrons in p -orbitals remain :
- (i) Paired, (ii) unpaired.
34. Electron in Bohr model of atom while moving in stationary orbit falls into the nucleus after sometime following a concentric path.
- (a) True, (b) False, (c) Don't know.
35. A $3d$ -electron is :
- (a) Less stable, (b) More stable than $4s$ -electron.
36. Fill in the blanks :
- (a) 1 mole of a gas at STP contains.....molecules,
 (b) 0.1 mole of oxygen contains.....particles,
 (c) 2.24 litres of a gas at STP is equal to.....mole.
37. (a) There are.....outer electrons in the carbon-12 atom, and ground state of electronic configuration of carbon atom is.....
 (b) The $1s$ and $2s$ -orbitals are.....in shape, while the three $2p$ -orbitals are.....in shapes.
 (c) All s -orbitals have.....shape and the shape of all p -orbitals can be represented by.....The size of an orbital is dependent upon the value of.....
 (d)quantum number accounts for the orientation of various orbitals in space.
 (e)quantum number represents the types of orbitals in a shell.
 (f) Atomic species having the same atomic numbers but different atomic masses are called.....
38. (a) An electron revolving in a closed orbit does not loose or gain any energy. In that state it is said to be in.....state.
 (b) The energy difference when the electron jumps from one level to the other is directly proportional to the.....Of the accompanying radiation.

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- (c) Transition from $n=2, 3, 4, 5$ to $n=.....$ is called Lyman series.
- (d) No two electrons in an atom have all the four quantum numbers.....
- (e) The allowed values of l in terms of n are.....
- (f) Two electrons in an orbitals must have..... spins.
- (g) According to Dalton's atomic theory, matter is composed of very small indivisible particles called..... However, we now know that they contain.....
39. (a) The atomic number of carbon is six. The number of protons in its nucleus will be.....
- (b) proposed that an atom consists of a positively charged nucleus surrounded by negatively charged electrons.
- (c) Since most of mass of an atom is concentrated in its nucleus, the latter must be made up of..... and.....
- (d) Neutrons and protons have almost identical masses, but the mass of an electron is..... times smaller than that of a proton. Thus, the mass of an atom is essentially due to its..... and.....
- (e) Since an atom is electrically neutral, the atomic number is also equal to the number of.....
- (f) The principal and azimuthal quantum numbers of the electron in the $2p$ -orbital are..... and..... respectively.
- (g) The spin quantum number can have value (s) of.....
- (h) The maximum number of electrons that can be accommodated in s -sub-shell is....., p -sub-shell is....., d -sub-shell is..... and f -sub-shell is.....
- (i) The electronic configuration of fluorine atom (At. No. 9) is represented as..... and it has..... unpaired electrons.

(C) Problems :

40. Calculate the number of moles of the respective particles in each of the following amounts of materials :

- (i) 10g of CaCO_3 , (ii) 6.023×10^{24} molecules of oxygen, (iii) 1.6 gram atom of oxygen, (iv) 2.24 litres of oxygen at STP (Atomic mass of C=12; O=16; Ca=40).

(Ans. (i) 0.1 mole, (ii) 10 moles, (iii) 0.1 mole, (iv) 0.1 mole).

41. (a) Calculate the mass of one molecule of oxygen (Avogadro's number $= 6.02 \times 10^{23}$; atomic mass of O=16).

(Ans. 5.3×10^{-23} g)

- (b) How many atoms and how many grams atoms are there in 20g of calcium? (Atomic mass of Ca=40).

(Ans. 3.0115×10^{23} atoms; 0.5 g atom).

42. Calculate the volume occupied at STP by :

- (i) 16g of oxygen, (ii) 5 moles of oxygen, (iii) 6.023×10^{24} molecules of oxygen.

(Ans. (i) 11.2 litres, (ii) 112 litres, (iii) 224 litres.)

43. Which of the following weighs most ?

(a) 1 mole of Na_2CO_3 ,

(b) 10 gram mole of hydrogen,

- (c) 12 gram atom of helium,
 (d) 6.023×10^{24} atoms of oxygen,
 (e) 22.4 litres of CO_2 at STP (Atomic masses of Na=23 ; C=12 ;
 O=16 ; N=14 ; He=4).

(Ans. 6.023×10^{24} atoms of oxygen).

44. What is the frequency of a radiation of visible light having a wave length of 4000 \AA ?

(Ans. $7.5 \times 10^{14} \text{ Hz}$).

45. Calculate the energy of photons of radiations having the frequency $5 \times 10^{14} \text{ sec}^{-1}$ (Planck's constant, $h = 3.99 \times 10^{-31} \text{ kJ sec mol}^{-1}$).

(Ans. $199.5 \text{ kJ mol}^{-1}$).

46. Calculate the wave-length of de Broglie wave associated with an electron moving at a velocity of $1.2 \times 10^9 \text{ cm sec}^{-1}$ (Mass of electron = $9.1 \times 10^{-28} \text{ g}$; $h = 6.625 \times 10^{-27} \text{ erg-sec.}$).

(Ans. 0.605 \AA)



The Periodic Classification of Elements

3.1. INTRODUCTION

The known 105 elements vary greatly in their physical and chemical properties and in the nature of the compounds which they form. The study of the individual properties and compounds of the elements would prove to be extremely laborious and time consuming. Although every element is different from every other element, similarities make possible groupings that simplify study. So, since long it has been the endeavour of the scientists to arrange the facts of elements in a systematic way so as to learn the maximum about them with least possible effort. The problem was the selection of an ideal on the basis of which their classification could be made.

In 1815, **Prout** suggested that "*all elements are integral multiple of the principle element 'protyle' and are really made up of hydrogen atom.*" This so-called '**unitary theory**' was rejected on the ground that it could not explain the fractional atomic masses of quite a number of elements, e.g., chlorine=35.5.

In 1829, **Dobereiner** gave the "**Law of Triads**" according to which *the chemically alike elements could be arranged in group of three in which the atomic mass of the middle element was approximately the arithmetic mean of the two extreme elements*". Among these are the triads lithium, sodium and potassium; chlorine, bromine, and iodine; calcium, strontium and barium. However, this law was not followed up because only a limited numbers of elements could give such triads and failed to accommodate other elements resembling a lot with the triads.

In 1863, **Newland** gave the '**Law of Octaves**' according to which *if elements be arranged in ascending order of their atomic mass, the every eighth element was a kind of repetition of the first one either succeeding or preceding it, like eighth note in an octave of music.*"

For example :

<i>Sa</i>	<i>re</i>	<i>ga</i>	<i>ma</i>	<i>pa</i>	<i>dha</i>	<i>ni</i>
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl

Thus, Na was a kind of repetition of Li ; Mg was similar to Be and so on.

This law did not receive much attention, since it was not valid especially for elements of higher atomic masses. Moreover, the discovery of inert gases gave a further set-back to this law. With the inclusion of neon between fluorine and sodium, and of argon between chlorine and potassium and so on, it was the 9th element and not the 8th which was similar to the first.

3.2. MENDELEEV'S PERIODIC TABLE

In spite of the importance of the earlier contributions, the major portion of the credit for the development of the periodic system must go to the Russian, Dmitrii Ivanovich Mendeleev, and to the German, Julius Lothar Meyer. In 1869, almost simultaneously and working independently, both put forward the theory that "*the properties of elements are periodic function of their atomic masses.*" If elements possessed the same atomic masses e.g., the triad iron-cobalt-nickel (Fe-Co-Ni) then their properties were similar. An increase in atomic mass in passing from one element to another on the other hand, contributed a definite change in chemical and physical properties.

On the basis of the periodic law, Mendeleev constructed a *Periodic Table of Elements* in which the elements were arranged in horizontal rows (called *periods*) in order of their atomic masses and in vertical column (called *groups*) according to their resemblance in properties. The main criterion for judging the similarities in properties was similarities of the valencies of the elements as exhibited in their oxides, chlorides and hydrides. He found, for example, that there were eight types of oxides representable by the formulae R_2O , RO , R_2O_3 , RO_2 , R_2O_5 , RO_3 , R_2O_7 and RO_4 . Then, on writing down the elements in order of increasing atomic masses, he found that each element gave an oxide of one particular type. (When an element formed two or more oxides it was necessary to select the one most characteristic of the element e.g., sulphur trioxide, SO_3 , for sulphur). The elements thus arranged themselves into 8 groups (The noble gases were not then known).

While framing the periodic table, Mendeleev, left gaps in the table, to accommodate the hitherto undiscovered elements. With the discovery of many more elements, Mendeleev's original table have been modified and improved, yet it bears the same name. The main feature of periodic table are as follows :

(1) **Groups.** There are nine groups including VIII group of typical transitional elements, and zero group of rare gases. The normal groups I to VII are sub-divided into sub-group A and B. The elements placed on the left in the column constitute sub-group A; while those placed to the right in the column form sub-group B.

(2) **Periods.** There are seven periods in all. The first period consists of 2 elements (H and He) only. Periods second and third are short periods consisting of eight elements each. Periods fourth and fifth are long periods consisting of eighteen elements each, of which eight elements are normal; while the rest exhibit variable valency and have coloured ions and latter are called transition elements. Period sixth is also a long period consisting of 32 elements of which first eight are normal, next 10 are transitional and the remaining 14 are rare earths (or Lanthanides). Period seventh is incomplete consisting of 6 naturally occurring elements and 13 artificially prepared elements, called transuranic elements.

Uses of the Mendeleev's Periodic Table. Periodic classification of Mendeleev lead to great advancement in chemical knowledge. Its merits are manifold indeed. A few of them are :

(1) **Systematic study of elements :** It has made the study of 105 elements quite convenient. With its help we can know maximum possible with the least effort. The study of all elements have been simplified to the study of nine groups only. By simply knowing the position of an element in periodic table, we can predict about its properties with considerable accuracy.

(2) **Prediction of new elements :** Mendeleev while arranging elements in ascending order of their atomic masses had to leave gaps (*i.e.*, vacant spaces) at certain places so as to maintain symmetry of the periodic table. He regarded gaps as due to hitherto undiscovered elements. He boldly predicted the physical and chemical properties of missing elements from the properties of their neighbours. Later on when these elements were discovered their properties remarkably agreed with the predicted one (*See* Table 3.1). Thus, gallium germanium and scandium were discovered many years later, Mendeleev had predicted their existence. So we can say that Mendeleev's table has helped the discovery of new elements.

(3) **Determination of atomic mass :** From the position of the element in the periodic table its valency is known. Hence, its atomic mass, equal to chemical equivalent multiplied by valency, can be calculated. Thus atomic mass of beryllium, uranium, etc. were calculated in this manner.

Table 3.1. *Mendeleev's prediction of the properties of germanium (named Ecasilicon by Mendeleev).*

Property	Predicted by Mendeleev	Currently observed
1. Atomic mass	72	72.59
2. Specific gravity (g cm^{-3})	5.5	5.35
3. Melting point	High	1220K
4. Specific heat (cal deg^{-1})	0.073	0.074
5. Gram-atomic volume (cm^3)	13	13.5
6. Colour	Dark grey	Greyish white
7. Valence	4	4
8. Reaction with acids.	Should be slightly attacked by acids such as HCl, but should resist attack by alkalis such as NaOH.	Gets dissolved by neither HCl nor dilute NaOH, but is dissolved by concentrated NaOH.
9. Boiling point of the tetraethyl derivative	333K	358–360K
10. Specific gravity of the dioxide.	4.7	4.228
11. Specific gravity of the tetrachloride.	1.9	1.8443
12. Boiling point of the tetrachloride.	373K	357K

(4) **Correction of atomic masses :** At the time of Mendeleev, some elements were misfits in the table because of their wrong atomic mass knowledge. The atomic mass of beryllium was regarded as 13.5 (chemical equivalent=4.5 and valency=3) and evidently it should be placed between C (12) and N (14), where there was no place for it. Hence, Mendeleev being confident of his periodic law, gave beryllium a valency of 2, and its atomic mass to be $4.5 \times 2 = 9$ and therefore it was correctly placed between lithium and boron in II group above Mg. Similarly, atomic mass of indium was regarded as 75.8 (chemical equivalent=37.9; valency=2) but with this atomic mass it could not fit between As (75) and Se (79). Hence, Mendeleev assumed the element to be trivalent. This made the atomic mass 113.7 and the element was correctly placed between Cd (112) and Sn (119) in III group above lanthanum.

(5) **In research and industry :** Periodic table supplied much valuable information which helped in stimulating research work. Thus, relationship of Ni to Co, Fe and Cr to V, Mo to W suggests that various combinations of these may be of great use in making special alloys.

Drawbacks of Mendeleev's Table : In spite of its useful role in the study of chemistry, Mendeleev's table possessed many drawbacks. Some of these drawbacks are :

(1) **Position of hydrogen :** Hydrogen is placed in group I-A

However, it actually resembles the elements of group I-A (alkali metals) as well as the elements of group VII-A (halogens). Thus, position of hydrogen in the periodic table is not clear.

(2) **Position of isotopes.** On the basis of atomic mass various isotopes of the same element should be assigned different places in the periodic table. However, this is not so in Mendeleev's table.

(3) **Position of lanthanides and actinides.** The fourteen elements following lanthanum (known as lanthanides or rare-earths) and the fourteen elements following actinium (known as actinides or transuranic elements) have not been provided separate and proper places in the Mendeleev's table, rather they have been placed in two rows at the bottom of the table.

(4) **Dissimilar elements placed together.** Noble metals Cu, Ag and Au are placed along with chemically dissimilar alkali metals in group I. Similarly, Mn possessing very few similarities with halogens have been placed in VII group.

(5) **Similar elements separated.** In the Mendeleev's table, certain chemically similar elements such as copper and mercury; gold and platinum have been placed in different groups.

(6) **Misfit anomolous pairs.** In the Mendeleev's table based on atomic mass, certain pairs e.g., argon (at. mass=39.94) and potassium (at. mass=39.1); cobalt (at. mass=58.94) and nickel (at. mass=58.59); tellurium (at. mass=127.67) and iodine (at. mass=126.27) would seem to be reversed in order of this basis.

3.4. MODERN PDRIODIC TABLE

Moseley (1913), who determined nuclear charge on the atoms of different elements, suggested that atomic number which expresses the structure is more fundamental property of the atom than atomic mass. This observation led to the modern periodic table, known as long-form periodic table. This is based on the 'Modern periodic law' which states that "*the properties of the elements and their compounds are a periodic function of the atomic number.*"

When the elements are arranged in order of increasing atomic numbers, elements with similar chemical properties reoccur at definite intervals, i.e., periodically. In regard to atomic structure, this periodicity is due to the periodicity in the number of electrons in the outer shells of the atoms of the elements. The electrons in the outermost shell of an atom are referred to as valence electrons. If elements having the same number of valence electrons are grouped together, the elements falling within each group are similar in chemical properties. Thus, *the periodic repetition or periodicity of properties of elements must be due to the repetition of similar*

s - Block (Representative Elements)		<u>MODERN</u> <u>PERIODIC TABLE</u>																p - Block (Representative Elements)											
Groups → I A		d - Block (Transition Elements)																VIIA 0											
Periods	1	H 1	II A																						H 1	He 2			
	2	Li 3	Be 4																					B 5	C 6	N 7	O 8	F 9	Ne 10
	3	Na 11	Mg 12	III B	IV B	VB	VI B	VII B	VIII			IB	II B	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18										
	4	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36										
	5	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54										
	6	Cs 55	Ba 56	La 57	Hf 72	Ta 73	W 74	Re 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86										
	7	Fr 87	Ra 88	Ac 89	Ku 104	Ha 105																							

f-Block (Inner Transition Elements)															
6	Lanthanide Series →	Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71
7	Actinide Series →	Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	No 102	Lw 103

electronic configuration of outermost energy levels of elements after certain intervals. In other words, elements having similar chemical properties and hence belonging to the same family (or group) have similar electronic configurations of their out-most orbit. For example, from the electronic configurations of alkali metals (IA group) it is clear that each member of the family possesses one electron in s -orbital of outermost orbit. In other words, valence orbits of alkali metals have the general configuration ns^1 , where n is the number of the valence energy level. Consequently, it is the presence of this single electron, in the outermost orbit, which is responsible for the similar properties of the alkali metals. Similarly, all members of the halogen family (VII-A group) have the general configuration ns^2, np^5 in the outermost energy level as shown below :

ELEMENT	ELECTRON CONFIGURATION
Fluorine ($9F$)	$1s^2 2s^2 2p^5$
Chlorine ($17Cl$)	$1s^2 2s^2 2p^6 3s^2 3p^5$
Bromine ($35Br$)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$
Iodine ($53I$)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4d^{10} 5s^2 5p^5$
Astatine ($85At$)	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4d^{10} 5s^2 5p^5 5d^{10} 6s^2 6p^5$

Owing to the presence of 7 electrons (s^2p^5) in the outermost orbit, each of the halogens has a tendency to gain 1 electron to acquire the stable configuration of the inert gas which just follows it. Consequently, this forms the basis of their similar properties.

Features of long-form Periodic Table. In the long-form periodic table the elements are arranged in order of their increasing atomic number, so that they fall into 18 vertical columns (families or groups) numbered IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB, IIIA, IVA, VA, VIA, VIIA and 0. The elements, in a given "A" group show some resemblances to the corresponding elements in the "B" groups of the same number.

There are seven horizontal rows referred as periods. The **first short period** of the table contains only the elements, hydrogen and the noble gas helium. Helium has a complete outer shell (K-shell) of two electrons.

The **second short period** contains eight elements, beginning with lithium and ending with the noble gas, neon. Neon has a complete outer shell (L-shell) of eight electrons.

The **third short period** contains eight elements beginning with sodium and ending with the noble gas, argon, which contains eight electrons in the outer shell (M-shell).

The *fourth period* is the first of two long periods that contain eighteen elements each. This period includes a series of elements from scandium (At. No. 21) through copper (At. No. 29), which are known as *first transition elements*, in which the second from the outer shell (the M-shell in this series) is building from eight to eighteen electrons. Before the transition series begins, however, two electrons enter the outer shell (the N-shell) in potassium (At. No. 19) and calcium (At. No. 20) respectively. Following the transition series the outer shell builds up, reaching eight electrons with the noble gas, krypton (At. No. 36).

The *fifth period*, beginning with rubidium and ending with xenon, is similar to the fourth period. It has eighteen elements and contains a second transition series from yttrium (At. No. 39) through silver (At. No. 47), in which the second from the outer shell (the N-shell) is building from eight to eighteen electrons, analogous to the first transition series in the preceding period.

The *sixth period* contains 32 elements. A third transition series is present, made up of lanthanum (At. No. 57) and the element hafnium (At. No. 72) through gold (At. No. 79), in which the second shell from the outside (the O-shell) builds from eight to eighteen electrons. Notice that the third transition series is split, however, between lanthanum and hafnium in a series of 14 elements—cerium (At. No. 58) through lutetium (At. No. 71). In these 14 elements the third shell from the outside (the N-shell which can hold a maximum of 32 electrons) builds from 18 to 32 electrons. Lutetium, therefore, has the structure 2, 8, 18, 32, 9, 2. These elements constitute the *first inner transition series* referred to as the *lanthanides* or the *rare earth elements*. Following lutetium, the elements hafnium through gold complete the third transition series, building the second from the outer shell (O-shell) up to 18 electrons. The outer (P-shell) then builds up reaching 8 electrons with the noble gas radon (At. No. 86).

The *seventh period* is incomplete. The first two members are francium (At. No. 87) and radium (At. No. 88) with K, L, M, N, O, P, and Q shells of 2, 8, 18, 32, 18, 8, 1 and 2, 8, 18, 32, 18, 8, 2 electrons, respectively. Actinium (At. No. 89), with the structure 2, 8, 18, 32, 18, 9, 2 is the first element of the fourth transition series. The next three naturally occurring elements (thorium, protactinium, and uranium) and the 11 transuranium elements, all artificially produced (neptunium, plutonium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, and lawrencium) constitute the second inner transition series, in which the third shell from the outside (O-shell) is building from 18 to 32 electrons. This series of elements (in which actinium is sometime included because of its similarity in properties) is called the actinide series.

Although only two elements (At. No. 104 and 105) beyond lutetium has been reported, it is logical to assume that these and any elements immediately beyond it (the elements 106, 107, 108, etc.) that may be produced will be a part of the fourth transition

series in which the second from the outer shell (the P-shell, in this case) builds toward 18 electrons.

Summary Classification of Elements in Terms of the Periodic Table. The periodic table, can conveniently be classified into four categories, according to their atomic structure.

1. **Noble gases or zero group:** Elements in which the outer shell is complete with eight electrons (two electrons for helium). Their outer electronic configuration is ns^2p^6 . The noble gases are helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn).

2. **Representative elements:** Elements in which the added electron enters the outermost shell and in which only the outermost shell is incomplete. The representative elements are those in groups IA, IIA, IIIA, IVA, VA, VIA and VIIA of the periodic table.

3. **Transition elements:** Elements in which the second shell from the outside is building from 8 to 18 electrons. The four transition series are:

(a) *First transition series:* Scandium (Sc) through copper (Cu).

(b) *Second transition series:* Yttrium (Y) through silver (Ag).

(c) *Third transition series:* Lanthanum (La); and hafnium (Hf) through gold (Au).

(d) *Fourth transition series* (incomplete). Actinium (Ac), kurochatovium (Ku), hahnium (Ha), 106.....

4. **Inner-transition elements:** Elements in which the third shell from the outside is building from 18 to 32 electrons. The two inner-transition series are:

(a) *First inner transition series:* Cerium (Ce) through lutetium (Lu).

(b) *Second inner transition series:* Thorium (Th) through lawrencium (Lw).

Note. Lanthanum and actinium, because of their similarities to the other members of the series are sometimes included as the first element of the first and second inner-transition series, respectively.

3.5. CLASSIFICATION OF ELEMENTS INTO *s*-, *p*-, *d*-, and *f*- BLOCKS

The elements, as arranged in the long-form of the periodic table, can also be classified into four blocks, known as *s*-, *p*-, *d*-, and *f*-, blocks. This classification is based on the name of the atomic orbital which receives the last electron.

s-block elements. Elements of groups I and II each having one and two electrons respectively in the s -orbital of their extreme orbits are together known as s -block elements. They have configurations ns^1 and ns^2 respectively where n denotes the outermost energy level. They do not have any electron in the $(n-1)d$ -orbitals, but their $(n-1)s$ and $(n-1)p$ orbitals are completely filled.

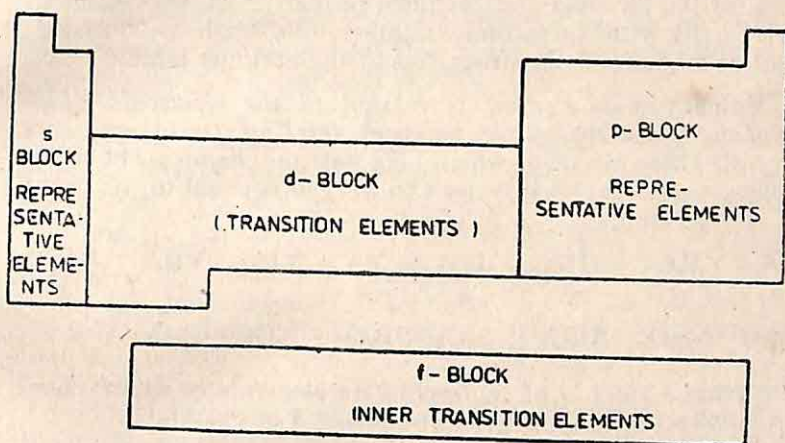


Fig. 3.1. Classification of elements into four blocks.

p-block elements. The elements of the groups IIIA, IV A, VA, VIA, VIIA and 0 have 3, 4, 5, 6, 7 and 8 electrons respectively in the outermost levels. They receive their last electron in their p -orbitals, namely, $2p$ -, $3p$ -, $4p$ -, $5p$ -, $6p$ -, and $7p$ -orbitals, respectively. Their outermost levels have the general configuration $ns^2, up^1; ns^2, np^2; ns^2, np^3; ns^2, np^4; ns^2, np^5; ns^2, np^6$ respectively. Their s -, p -, and d -orbitals of $(n-1)$ orbit are completely filled. In case of helium, the first element of zero group, the configuration is $1s^2$ since it has two electrons.

The elements of the s - and p - blocks are also collectively called as **representative elements**.

d-block elements. The elements lying between the s - and p -blocks are jointly known as d -block elements because their outermost energy levels remain incompletely filled; while the $(n-1)d$ -orbitals are progressively filled. Their general electronic configurations for the last two energy levels may be given $(n-1)s^2, (n-1)p^6, (n-1)d^{1-10}, ns^{0-2}$. The d -block elements are also known as transition elements because their properties are intermediate between those of s - and p -block elements.

f-block elements are elements in which the last electron enter the f -orbitals of their atoms. The last electron is added to the $(n-2)f$ -orbital while the two outermost orbits, i.e., n and $(n-1)$ remains incompletely filled. 14 lanthanides (cerium to lutetium) and 14 actinides (thorium to lawrencium) belong to this block. Inlanthanides, $4f$ -orbital and in actinides, $5f$ -orbitals are

progressively filled up, *f*-block elements are placed at the bottom of the periodic table. The *f*-block elements are also known as *inner-transition elements*.

3.6. PERIODICITY IN ATOMIC PROPERTIES OF ELEMENTS.

Most of the physical and chemical properties of the elements vary periodically with the atomic number. We shall now discuss the variation of some of the properties in the periodic table.

1. **Valency of an element is related to the electronic configuration of outermost energy (or valence) level of its atoms**, since it is generally these electrons which take part in chemical bonding. The valency of element with respect to oxygen is equal to its group number. For example :

0	IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIIIA
0	1	2	3	4	5	6	7	8
Nil	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	Cl ₂ O ₇	RuO ₄

The general valency of representative elements is either equal to group number or 8 minus group number. For example :

0	IA	IIA	IIIA	IVA	VA	VIA	VIIA
0	1	2	3	4	8-5=3	8-6=2	8-7=1
Nil	LiCl	BeCl ₂	BCl ₃	CH ₄	NH ₃	H ₂ O	HCl

The transition metals having 1 or 2 electrons in their ultimate shell exhibit variable valency, but their most common valency is 2.

2. **Atomic radius.** In ordinary sense, the atomic radius may be taken as the distance between the centre of the nucleus and the outermost shell of electrons. According to wave theory an electron, at times, may be very close to the nucleus while at other times it may be far away from the nucleus. There is always a probability of locating it even at a great distance from the nucleus. Consequently, there is no certainty with regard to the exact position occupied by

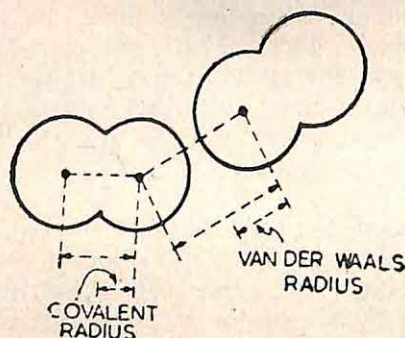


Fig. 3.2. Covalent and van der Waal's radii.

electron at any time. In spite of these limitations it is still possible to know the approximate radii of atoms by determining the distance between atoms in molecules. There are two concepts of atomic radius. These are : (i) "*van der Waals radius*" is one-half of the distance between the nuclei of two adjacent atoms belonging to the two neighbouring molecules of an element in the solid state. This is related to the effective packing size of the atom when the element is in solid state. (ii) "*Covalent radius*" is one-half of the distance between the nuclei of two atoms of the same element in a molecule bonded by a single bond (see Fig. 3'2).

It may be pointed out that the covalent radius is smaller than van der Waal's radius because in the formation of a covalent bond the atoms have to come closer to each other. For instance, the covalent and van der Waal's radius of hydrogen are 0.37\AA and 1.2\AA respectively. It may be emphasized here that inert gases do not form any covalent bonds. Therefore, in crystals of noble gases, van der Waal's forces are the only attractive forces prevailing in these.

Variation of atomic radii (covalent) in a period. The atomic radii decrease in moving from left to right in any given period. This is illustrated by atomic radii of elements of the second period :

Element	Li	Be	B	C	N	O	F
Atomic number	3	4	5	6	7	8	9
No. of energy levels	2	2	2	2	2	2	2
Atomic radius (\AA)	1.34	0.90	0.82	0.77	0.75	0.73	0.72

The variation of atomic radii in a period is explained on the basis of electronic configurations of elements. As we move from left to right in a period the atomic number and hence the nuclear charge increases progressively (from +3 to +9 in case of second period), but the number of energy levels accommodating these electrons remain the same (2 in case of 2nd period). The result is that the electrons are attracted more and more strongly towards the nucleus due to increased nuclear charge. In this way, the atomic size gradually contracts in moving from left to right across a period.

Variation of atomic radii in a group. In moving from top to bottom in a group, the atomic radii increase. In moving down in a group, two opposing effects are encountered. The number of main energy level increases and, therefore, the outermost electrons are located at greater distance from the nucleus. On the other hand, there is a greater pulling in the electron shells on account of increasing nuclear charge. But increase in size by the addition of a new shell is larger than the contractive effect of the increasing nuclear charge. The net effect is increase in atomic radii in moving from top to bottom in a group. The trend is illustrated by taking the example of IA group.

Element	At. No.	Nuclear Charge	No. of main energy levels	Atomic radius (Å)
Li	3	+3	2	1.33
Na	11	+11	3	1.54
K	19	+19	4	1.96
Rb	37	+37	5	2.16
Cs	55	+55	6	2.35

3. Atomic volume. "Gram-atomic volume" may be defined as the volume occupied in the solid state by one gram-atom of the element at its melting point. Since one gram-atom contains 6.023×10^{23} atoms, so, atomic volume gives an idea of the size of a single atom.

Variation of atomic volume in a period. There is no clear pattern in the variation of gram atomic volume in a period, as is evident from the values for second period elements. This is due to the fact that gram-atomic volume of an element is greatly

Element	Li	Be	B	C	N	O	F
Gram-atomic volume (cm ³)	13	5	5	5	14	11	15

influenced by the packing arrangement of its atoms in the solid state. Different elements have different packing arrangements of their atoms in the solid state, so it is not possible to compare atomic volumes in a simple manner.

Variation of atomic volume in a group. In moving down a group the gram atomic volumes go on increasing gradually in the same way as atomic radii. This is evident from the values of 1-A group shown below.

Element	Li	Na	K	Rb	Cs
Gram-atomic volume (cm ³)	13	24	46	56	77

4. Ionic radii. The neutral atom on losing or gaining one or more electrons change into a positive ion (cation) or negative ion (anion). The effective size of these ions is expressed in terms of ionic radius. Ionic radius may be defined as the distance from

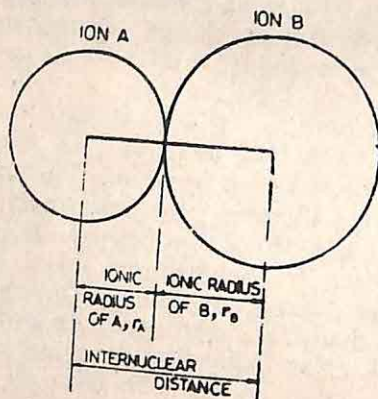


Fig. 3.3. Illustration of ionic radius.

the nucleus of an ion upto which it has influence on its electron cloud. The intermolecular distance in any compound (as determined by X-ray measurement) is considered to be the sum of the radii of the two ions involved (see Fig. 3.3). Knowing the radius of one, that of the other can be calculated.

The ionic radii exhibit the following general trends.

(i) *The radius of positive ion (cation) is smaller than that of the corresponding atom.* This is because a cation is formed by the loss of one or more electrons from an atom. This generally causes the removal of the whole of the outer shell of electrons so that the cation left is smaller in size. For example :

Electronic	Na	→	Na ⁺ + e ⁻
Configuration	(2,8,1)		(2,8)
No. of shells	3		2
Electronic	Mg	→	Mg ²⁺ + 2e ⁻
Configuration	(2,8,2)		(2,8)
No. of shells	3		2

Moreover, with the elimination of one or more valence electrons, the effective nuclear charge (i.e., ratio of positive charge on the nucleus to the number of orbital electrons) is increased. This causes more pulling of the electrons towards the nucleus, thereby resulting in the decrease of the size of the positive ion. The following data illustrates the comparative sizes of atoms and cations formed by them.

Atomic radius (Å)	Ionic radius (Å)
Na = 1.54	Na ⁺ = 0.95
Mg = 1.36	Mg ²⁺ = 0.65
Al = 1.25	Al ³⁺ = 0.50
Mn = 1.26	Mn ⁴⁺ = 0.46

(ii) *The radius of an anion (or negative ion) is larger than that of the corresponding atom.* This is shown below :

Atomic radius (Å)	Ionic radius (Å)
Cl = 0.99	Cl ⁻ = 1.31
O = 0.74	O ²⁻ = 1.40
S = 1.02	S ²⁻ = 1.84
N = 0.75	N ³⁻ = 1.71

During the formation of a negative ion, one or more electrons are added to the atom ; whereas the nuclear charge remains the same. As a result the effective nuclear charge is reduced and the

electron cloud experience lesser pull by nucleus. In other words, the electron cloud expands due to greater freedom of getting away from the nucleus. An anion, therefore, is invariably larger than that of the corresponding atom.

(iii) In moving down a group, the ionic radii go on increasing gradually in the same way as atomic radii.

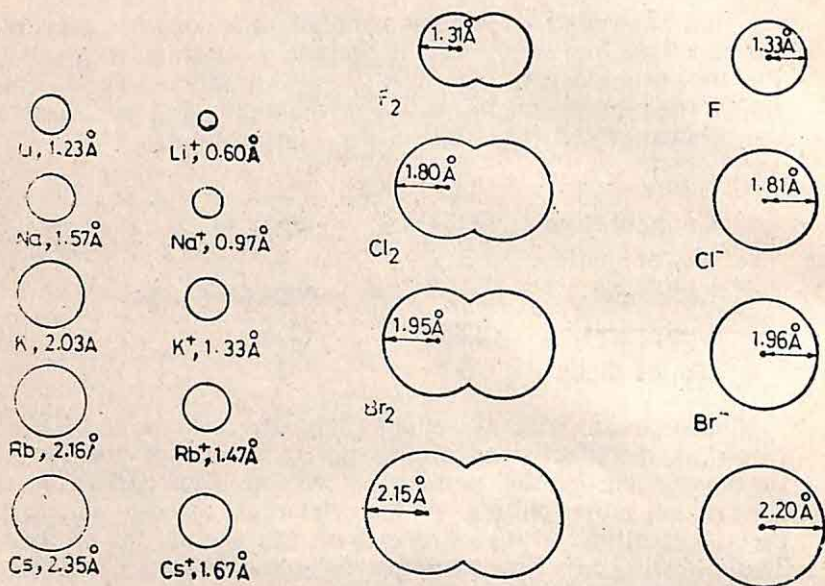


Fig. 3.3.

(iv) Ionic radii of iso-electric ions (i.e., ions of different elements having the same number of electrons) decrease with increase in atomic number since their effective nuclear charge increase. For example :

Ion	N ³⁻	O ²⁻	F ⁻	Na ⁺	Mg ²⁺
No. of electrons	10	10	10	10	10
Nuclear charge	+7	+5	+9	+11	+12
Radius (Å)	1.71	1.40	1.36	0.95	0.60

(5) **Ionization energy.** The ionization energy (E) of an element is defined as the energy required to remove the most loosely bound electron from an isolated atom in the gaseous state resulting in the formation of a positive ion.



Evidently, the smaller the value of ionization energy (E) the easier it is for the neutral atom to form cation. Ionization energy is generally expressed in eV atom^{-1} (electron volt per atom) or kJ mol^{-1} ($1 \text{ eV atom}^{-1} = 96.3 \text{ kJ mol}^{-1}$).

Ionization energies are generally determined by spectroscopic techniques or by passing a gradually increasing intensity electric current through the vapour of the element in a discharge tube.

If first electron is removed, then the energy required is called the *first ionization energy* (E_1). If the second electron is removed from M^+ to M^{2+} state, then, the energy required is called the *second ionization energy* (E_2), and so on. The general trends in the variation of ionization energy are listed below.

(i) *Ionization energy decreases from top to bottom in a group.* Since atomic size increases on moving down a group, it is evident that outer electrons in larger atoms lie farther from the nucleus and hence it is easier to knock out one of them. For example ;

Group I-A	Li	Na	K	Rb	Cs
E_1 (kJ mol ⁻¹)	520	495	418	403	374

(ii) *The ionization energy increases from left to right in a period* since the effective nuclear charge increases and the electrostatic attraction holding the outer electrons toward the nucleus increases with the increase in the nuclear charge. Hence, greater energy is needed to pull out more strongly attracted electron from the atom. For example :

Period 2 elements	Na	Mg	Al	Si	P	S	Cl	Ar
E_1 (kJ mol ⁻¹)	495	737	577	735	1062	999	1254	1519

(iii) Within a given shell, the binding energy of electrons in various sub-shells is in the order $s > p > d > f$, since s -electrons are relatively nearer to the nucleus than p -electrons of the same shell. This accounts for lower ionization energy of Al (577 kJ mol⁻¹) compared to Mg (737 kJ mol⁻¹) since removal of a p -electron from Al to produce Al^+ ion is easier than the removal of an s -electron of Mg to produce Mg^+ ion.)

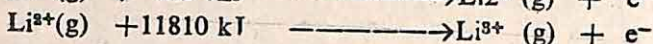
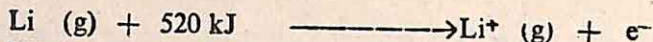
(iv) *Ionization energy of inert gases is highest in their respective period* since it is difficult to break the stable $s^2 p^6$ arrangement occurring in them.

(v) It is more difficult to extract an electron from exactly half-filled sub-shells. Thus, N with $2p$ - sub-shells, each half-filled has a greater ionization energy than elements on its sides (i.e., C and O),

Element	C	N	O
Configuration	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$	$1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$
E , (kJ mol ⁻¹)	1086	1403	1314

(vi) Second and third ionization energies of an element are always greater than its first ionization energy because it becomes progressively more difficult to remove an electron from positively charged residue. For example :

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first (E_1), second (E_2) and third (E_3) ionization energies of lithium are 520, 7297, and 11810 kJ mol⁻¹, respectively.

(6) **Electron affinity.** Just as ionization energy measures the tendency of an atom to form cation, the electron affinity gives a measure of the tendency of an atom to form an anion. It is defined as the energy released when a neutral atom in the gaseous state take up an extra electron to form a negatively charged ion i.e.,



Thus, electron affinity of an atom measures the tightness with which it binds an additional electron to itself.

It is rather difficult to determine electron affinities experimentally and consequently their values are known only for a few elements. The available data indicates the following trends.

(i) *Electron affinities of noble gases are zero* because all of them have stable s^2p^6 configuration and there is no chance for the addition of an extra electron.

(ii) *Electron affinities of halogens (group VII-A) are far the highest* due to their high tendency to gain an additional electron to yield stable s^2p^6 configuration.

(iii) *Electron affinities decreases in going from top to bottom in a group* since the effective nuclear attraction for the electrons decrease due to increased atomic size.

VII-A group element	F	Cl	Br	I
Electron affinity (kJ mol ⁻¹)	333	348	340	297

Exceptionally low value for fluorine is possible due to the strong electron-electron repulsion associated in the relatively compact $2p$ -sub-shell.

(iv) *Electron affinities increase in going from left to right across a period.* On moving across a period, the atomic size decreases and hence the force of attraction exerted by the nucleus on the electron increases. Consequently, the atom will have a greater tendency to attract the additional electron. For example.

Period 2 element	Na	Si	S	Cl
Electron affinity (kJ mol ⁻¹)	80	134	197	348

QUESTIONS

(A) Essay Type :

1. (a) What is a Dobereiner's triad ? Give one example.
(b) What are the essential features of the periodic table of elements by Mendeleev ? What are the defects of this table ? Discuss how this table has been modified subsequently.
2. What is long-form of the periodic table ? What are its main features ? How is it superior to Mendeleev's table ? Give at least four points.
3. What is meant by the term periodic classification of elements ? In what way Mendeleev's periodic table was helpful to chemists ? Give 2 points.
4. Write a comprehensive essay on modern classification of elements.
5. Explain the classification of elements into *s*, *p*, *d*, and *f*-blocks laying stress on the basis of this classification.
6. Write notes on :
(a) Representative elements.
(b) Inert gases.
(c) Transition elements.
(d) Inner transition elements.
7. What do you understand by the term ionization energy ? How do the ionisation energies of the elements vary in the periodic table ? Explain various factors which govern the ionisation energy.
8. What is meant by atomic radius and ionic radius ? How does atomic radius change across a period and down a group ? Give reasons for these changes.
9. Explain why the electron affinities of the atoms increase from left to right along a horizontal row in the periodic table ?
10. Explain the following, giving reasons.
(a) Second ionisation potential is always higher as compared to its first ionisation potential.
(b) The size of Cl^- ion is larger than Cl atom ; while that of Na^+ ion is smaller than that of Na atom.
(c) The ionisation potential of transitional elements is almost constant.
11. What is meant by electron affinity of an element ? In the second period why is the electron affinity for nitrogen found to be less than what it should be :

$$C=1.13, N=0.20, O=1.48.$$

(B) Objective Type :

12. Which of the following correctly states the modern periodic law ?
(a) When elements are arranged in an increasing series of atomic mass, elements with similar properties recur at intervals of seven.
(b) The properties of the elements are periodic function of their atomic masses.
(c) The properties of the elements are periodic functions of their atomic numbers.
(d) When a group of three similar elements are arranged in the order of their increasing atomic masses, the atomic mass of the second element is approximately equal to the average of atomic masses of the other two elements
13. Select the correct statement(s). The atoms of the elements belonging to the same group of the periodic table all have the same
(i) number of protons,
(ii) number of neutrons,

- (iii) number of electrons,
- (iv) number of electrons in the outer-most sub-shell,
- (v) size.

14. Select the correct statements.

- (a) All alkali metals have one electron only in their respective outer-most energy shell.
- (b) Inert gases have the general [electronic configuration $ns^2 np^6$, where n is the number of outermost energy shell.
- (c) The s , p , d and f -block of elements are also called the representative elements.
- (d) Transition elements have their last two shells incomplete.
- (e) Inner transition elements have their last three shells incomplete.
- (f) The radius of Na^+ ion is less than that of Na atom.
- (g) The ionisation potential of fluorine is less than that of chlorine.
- (h) When cations are formed from neutral atom ionic radius decreases.
- (i) When anions are formed from neutral atom ionic radius increases.

15. Choose the correct answer.

- (a) Which element has the lowest first ionisation potential ?
(i) Li, (ii) Be, (iii) F, (iv) Ne.
- (b) Which element has the highest first ionisation potential ?
(i) Li, (ii) Na, (iii) K, (iv) Rb, (v) Cs.
- (c) Which element has the highest atomic radius ?
(i) H, (ii) Li, (iii) Na, (iv) K, (v) Rb.
- (d) Which cation has the highest ionic radius ?
(i) Na^+ , (ii) Mg^{2+} , (iii) Al^{3+} .

16. Fill in the blanks :

- (a) Chemical properties of elements are periodic function of their.....
- (b) Inert gases have the general electronic configuration.....
- (c) Combined s - and p - block of elements are called.....elements.
- (d) Ionisation potential of sodium is.....than that of magnesium.
- (e) Electron affinity.....along a period.
- (f) Sodium ion has.....radius than chlorine ion.
- (g) d -block elements are placed in between.....and.....block elements.
- (h) f -block elements are called.....elements.
- (i) Electron affinities of.....group elements is zero.
- (j) Second ionisation energy of an element is always.....than that of its first ionisation energy.

17. Match the following :

List A

- (1) s -block element
- (2) Chlorine ion has a
- (3) f -block elements are called
- (4) d -block elements are placed in between.
- (5) Sodium ion has a
- (6) p -block element

List B

- (a) Inner transition element.
- (b) Sodium.
- (c) s - and p -block elements.
- (d) p - and f -block elements.
- (e) Smaller radius than that of chlorine atom.
- (f) argon

- (7) Modern periodic table is based on
- (8) The second ionization energy is always higher than the first ionisation energy because the
- (g) same radius as that of sodium atom.
- (h) larger radius than that of chlorine atom.
- (i) larger radius than that of sodium atom.
- (j) transition elements.
- (k) smaller radius than that of sodium atom.
- (l) chlorine.
- (m) atomic numbers.
- (n) electronic configurations.
- (o) electron is more highly bound to the nucleus in an ion.
- (p) electrons are attracted more by the core electrons.
- (q) ion become more stable, attaining octet or duplet configuration.



Chemical Bonds and Molecules

4.1. INTRODUCTION

The number of elements known at present are only 105, but the total number of chemical substances known is well over a million. Most of the substances exist in the form of molecules. Molecule is an electrically neutral cluster or aggregate of atoms in which atoms are held together by mutual attraction. *The attractive forces which hold together the constituent atoms in a molecule (or any other chemical species) is known as a "chemical bond"*. For example, hydrogen gas (H_2) exists in the form of molecules each of which consists of two hydrogen atoms bonded together. Water vapour molecule (H_2O) consists of two hydrogen and one oxygen atom bonded together. Sulphur in solid state (S_8) consists of aggregates of eight sulphur atoms bonded to one another. In diamond, a very large number of carbon atoms are bonded together to form a giant molecule. In sodium chloride, the constituent units are Na^+ and Cl^- ions, which are strongly held together throughout the crystal. Thus, it is clear that different substances have been formed by different kinds of combinations involving atoms of the same and/or different elements.

4. CAUSE OF CHEMICAL BONDING

It appears that a bonded state is more stable and, therefore, has lower potential energy than that of unbonded atoms. Hence, *chemical bond is formed between atoms only if potential energy of the system undergoes a fall*. On the other hand, if there is no fall in potential energy of the system, no bonding is possible. Thus, we can generalise that *the process of chemical bonding is always accompanied by a decrease of energy, and greater the decrease of energy in the bond formation, the greater is the strength of the bond*.

The first rational explanation for the formation of chemical bonds was based on the study of the electronic configuration of noble or inert gases. The study of spectra of inert gases of zero

group revealed that they are quite stable and do not combine chemically with any other element or with each other. The electronic configurations of these inert gases are given below :

ELEMENT	ELECTRON CONFIGURATION
Helium (${}^2\text{He}$)	$1s^2$
Neon (${}^{10}\text{Ne}$)	$1s^2$ $2s^2$ $2p^6$
Argon (${}^{18}\text{Ar}$)	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$
Krypton (${}^{36}\text{Kr}$)	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$
Xenon (${}^{54}\text{Xe}$)	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $5s^2$ $5p^6$
Radon (${}^{86}\text{Rn}$)	$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $3d^{10}$ $4s^2$ $4p^6$ $5s^2$ $5p^6$ $5d^{10}$ $6s^2$ $6p^6$

Thus, all noble gases in their outermost shell have the s^2p^6 configuration (except helium which has one shell only with configuration $1s^2$). Based on this Lewis and Kossel (1916) put forward "electronic concept of chemical bonding". Accordingly, *atoms of various elements combine with one another by undergoing electronic rearrangement so as to acquire stable noble gas configuration of 8 (s^2p^6) electrons in their outermost shell.* This simple explanation is known as octet rule. However, this concept has been suitably extended so as to furnish a complete picture of chemical bonding.

4.3. TYPES OF BONDS

It may be recalled that bonding between closely approaching atoms can take place if the process results in the lowering of energy of system. However, this lowering of energy and consequent bond formation may take place in different ways depending upon the electronic configuration of combining atoms. According to their mode of formation, the different types of bonds may be classified as : (i) ionic bonds, (ii) covalent bonds, (iii) co-ordinate bonds, and (iv) metallic bonds.

In addition to the above main types of chemical bonds, there can be attractive interactions known by the name hydrogen bond and van der Waal's interactions.

4.4. IONIC BOND

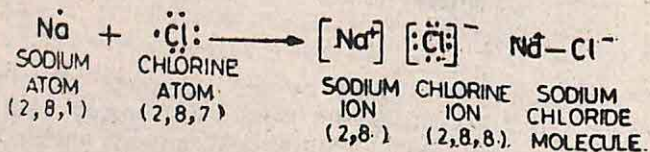
An ionic bond is formed by the complete transference of one or more electrons from the outermost energy shell (called, valency shell) of one atom to outermost energy shell of another dissimilar atom, so that both acquire stable inert gas configuration. The atom which loses the electrons acquires a positive charge and becomes what is called, positive ion. On the other hand, the other

atom which gains electrons acquires a negative charge and becomes what is called, a negative ion. These two oppositely charged ions combine due to electrostatic force of attraction to form an electrovalent or ionic compound. It may be pointed here that electrostatic attraction always tends decrease the potential energy.

Conditions for the formation of ionic bonds. Formation of an ionic bond depends upon ionization energy and electron affinity of the atoms involved. *One of the atoms should have a low ionization energy so that only a small amount of energy is required to pull out an electron from its outermost energy level. On the other hand, the other atom should have a high electron affinity so that it can readily accepted an electron in its outermost energy level.*

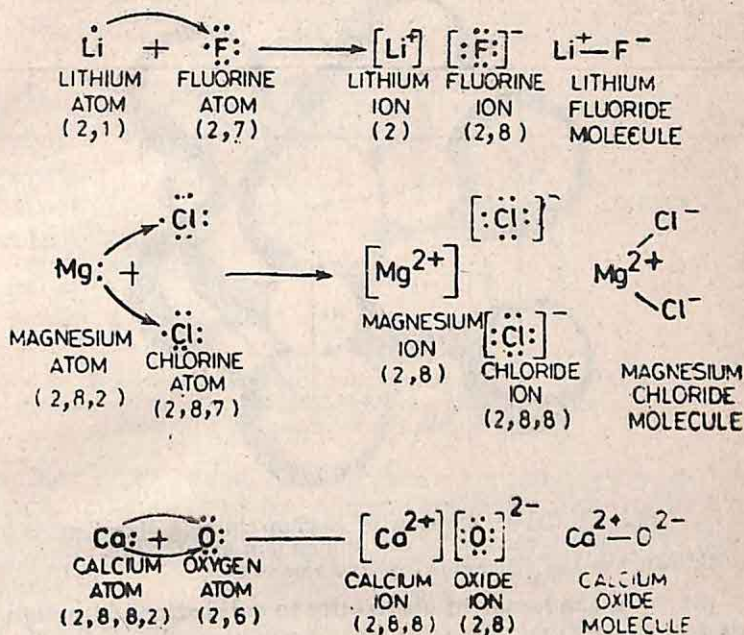
Alkali metals (group IA) have low ionization energies and halogens (Group VII A), on the other hand, have high electron affinities. Consequently, an atom of alkali metal will readily combine with a halogen atom to form an ionic bond. This prediction is actually found true. Thus, when a piece of sodium consisting of a vast number of sodium atoms is burnt in chlorine we get crystals of sodium chloride consisting of a large number of Na^+ and Cl^- ions. Alkaline earths (group IIA) also have low ionization energies, they also form cations but not so readily as alkali metals. The elements of VIA group also have good electron affinities so, they also form ionic compounds.

Examples of ionic bond formation: Let us consider the formation of sodium chloride. When a sodium atom (At. No. 11, electronic configuration 2,8,1, or $1s^2; 2s^2p^6; 3s^1$) and a chlorine atom (At No. 17; electronic configuration 2,8,7 or $1s^2; 2s^2p^6; 3s^2p^5$) approach each other, an electron is transferred from sodium to chlorine atom yielding oppositely charged sodium ions (Na^+) and chloride ions (Cl^-) respectively. These ions are held together by the force of electrostatic attraction between oppositely charged ions. Ionic bond formation is represented in terms of Lewis dot formula. In this scheme, an atom is represented by the symbol of the element and electrons in the outer (valency) shell, which alone are involved in chemical bonding, are represented by dots (.). Thus, each dot represents a single electron in the valency shell. The above cited example of sodium atom and a chlorine atom and their combination to form sodium chloride is represented as under :



The number of electrons lost or gained by an atom is called the **electrovalency** of the atom. Thus, **electrovalency** of sodium is

+1; while that of chlorine is -1. Some other examples of electrovalent bond formation are given below :



4.5. PROPERTIES OF IONIC COMPOUNDS

(1) **Non-directional nature.** Ionic compounds are made up of oppositely charged ions. Each ion is surrounded by an uniformly distributed electric field. So they are non-directional and cannot exhibit space isomerism.

(2) **Crystal structure.** X-ray diffraction studies of ionic compounds, show that the oppositely charged ions are not joined to form simple individual molecules. On the other hand, *each ion is surrounded by a large number of oppositely charged ions*. Moreover, cations and anions, having strong electrostatic forces of attraction, are arranged in a definite geometric pattern. *Such a regularly ordered three-dimensional arrangement of particles (ions) is known as a crystal.* The actual crystal structure is determined by the charges and the sizes of the ions concerned. For instance, in case of sodium chloride the crystal has structure in which each Na^+ ion is surrounded by six Cl^- ions, and each Cl^- ion is surrounded by six Na^+ ions as shown in Fig. 4.1.

The formula of an ionic compound merely indicates the relative numbers of each type of ion present in the crystal.

Thus, the formula NaCl simply shows that in sodium chloride crystal there is one Na^+ ion for every Cl^- ion and vice-versa.

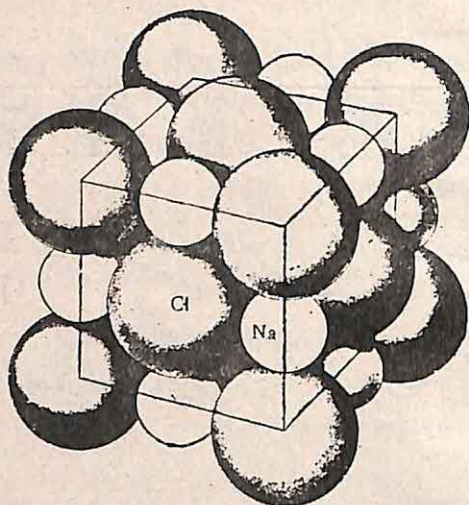


Fig. 4.1. Crystal structure of sodium chloride, showing the arrangement of six sodium ions around one chloride ion and vice versa.

(3) **Non-conductor of electricity in solid state.** Although ionic solids consist of ions, yet they do not conduct electricity since the electrons of each ion are held very tightly to the nucleus and the ions themselves due to electrostatic forces. Consequently, ions in these solids remain intact occupying fixed positions in the crystal. When an electric field is applied to ionic solid the tightly held ions are unable to move to any appreciable extent and therefore, no current flows.

(4) **Conductor of electricity in molten state.** As the temperature is raised, an increase in kinetic energy of the constituent ions takes place. When the substance goes into the molten state, the increased kinetic energy of the ions is large enough to overcome the attractive forces and the ions become mobile and are thus free to move under the influence of applied voltage. The ionic substances are consequently, able to conduct electricity in the molten state.

(5) **High melting and boiling points.** On account of strong electrostatic forces of attraction existing in ionic solid a considerable energy is needed to overcome these forces and break down the crystal lattice. Hence, such compounds have high melting and boiling points.

(6) **Solubility in water.** Ionic solids are soluble in water and other polar solvents having high dielectric constants. This high dielectric constant of the solvent cuts off the electrostatic forces of attraction between the ions, thereby they tend to be

separated (see Fig. 4.2). Moreover, the interaction between the polar solvent molecules and the ions further helps the dissolution process. These free ions are able to move under the influence of an electric field and thus can act as carriers of current.

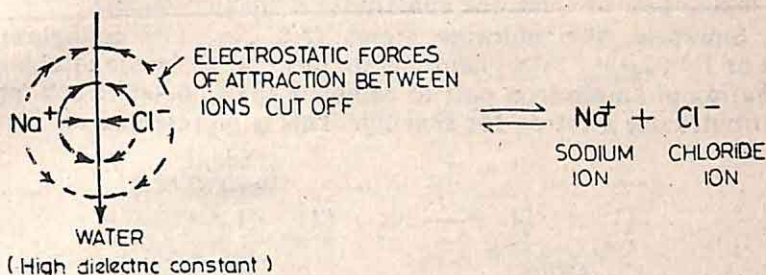


Fig. 4.2. High dielectric water cuts off the electrstatic forces of attraction between ions of sodium chloride, thereby producing free sodium and chloride ions.

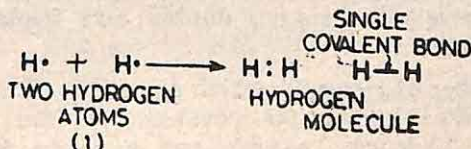
On the other hand, the organic solvents (like carbon tetrachloride, ether, etc.) are almost non-polar and have low dielectric constants and hence they are unable to separate ionic compounds into ions. Consequently, *ionic compounds are generally insoluble in organic solvents.*

(7) **Ionic reactions.** The reactions involving these substances usually take place between ions rather than molecules.

4.6. COVALENT BOND

There are many substances which cannot be formulated with ionic bonds, either because they are non-electrolyte (*i.e.*, they do not conduct electricity, even when dissolved in water) *e.g.*, tetrachloro methane (CCl_4) or because the atoms bonded together are same, so that neither would be expected to transfer an electron to the other *e.g.* hydrogen H_2 .

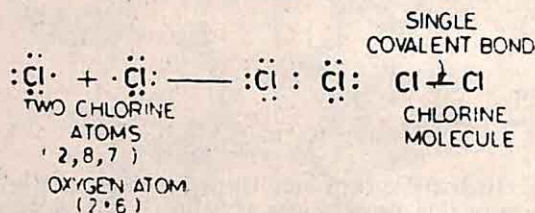
To account for the formation of such molecules, Lewis, in 1916, suggested that atoms might attain a noble gas structure, not by complete transference of electrons as in ionic bonding, but by sharing electrons. *This kind of bond formed by the mutual sharing of electrons between the atoms of the same or different element, is called covalent bond.* For example, let us consider the formation of the hydrogen molecule from two hydrogen atoms. Each hydrogen



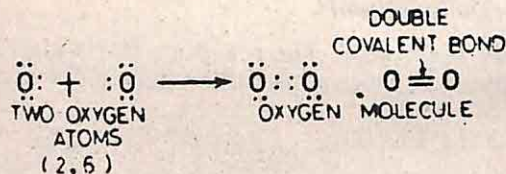
atom (At. No. 1; configuration $1s^1$) has one electron in its first and only shell. The two combining atoms, thus, contribute one electron pair as shown in terms of Lewis dot formula.

The mutually shared pair of electrons enable both the hydrogen atoms to acquire the stable configuration of helium gas. The shared pair of electrons constitutes a covalent bond.

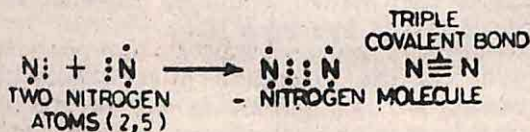
Similarly, two chlorine atoms (At. No. 17; configuration 2,8,7 or $1s^2$; $2s^2p^6$; $3s^2p^3$) combine to form a molecule of chlorine by sharing of an electron pair to complete their octet. Each atom contributes one electron for sharing. This is represented as :



Two oxygen atoms (At. No. 8; configuration 2,6 or $1s^2$; $2s^2p^4$) combine to form oxygen molecule by sharing two pairs of electrons between them. This is because each atom has 6 electron in its valence shell and requires 2 more to complete its octet and acquire stable configuration.



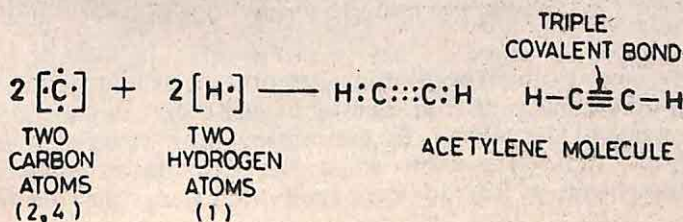
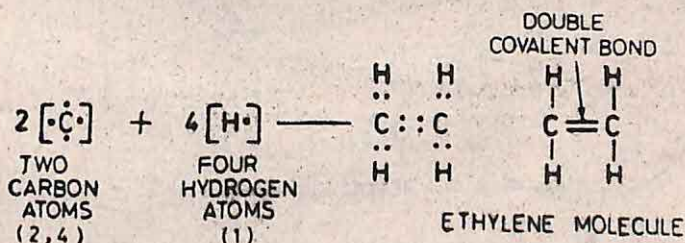
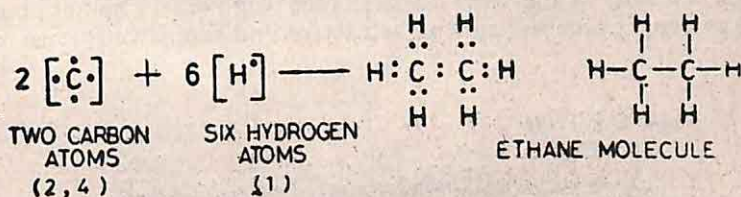
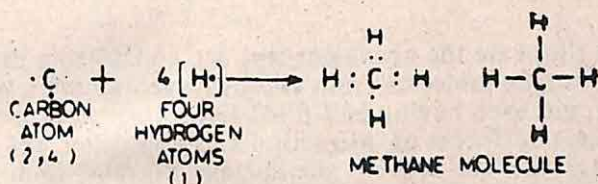
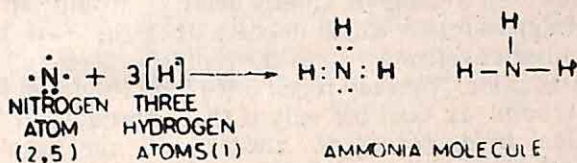
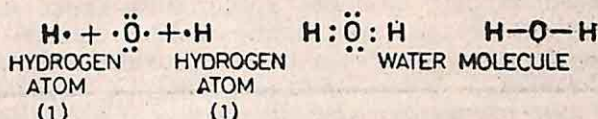
In the same way two nitrogen atom (At. No. 7; configuration 2,5 or $1s^2$; $2s^2p^3$) form nitrogen molecule by sharing three pairs of electrons between them.



A shared pair of electrons represents one covalent bond or single bond. Similarly, a covalent bond is known as double or triple bond when two or three electron pairs are shared between two atoms. The single, double and triple bonds are generally denoted respectively by a single, double and triple lines between the atom concerned.

The number of electrons which an atom of an element can share with others is known the covalency of the element. Thus, covalencies of hydrogen, oxygen and nitrogen are 1, 2 and 3 respectively.

Some more examples of covalent bond formation are given below :



4.7. ORBITAL CONCEPT OF COVALENT BOND

A very simplified picture of covalent bond formation by sharing of electron pair does not give an idea about the actual process and the various forces operating in the molecule. A clear picture to understand these aspects is provided by the **orbital concept of bonding**. According to this concept a *covalent bond is formed between two atoms when an electron of half-filled valence orbital of one atom overlaps with an electron with opposite spin belonging to half-filled valence orbital of another*. It should be remembered that the overlap of atomic orbitals would be possible only if the attractive forces which operate when the two atoms approach each other are stronger than the repulsive forces so that the net result is attraction. We may recall once again that the formation of a chemical bond is possible only if the approach of the atom is accompanied by decrease of energy. If the net result is attraction, total energy of the system decreases and a chemical bond results.

Let us illustrate the above concept by considering the formation of a hydrogen molecule from two hydrogen atoms. When two hydrogen atoms, each having half-filled $1s$ -orbital, approach closer to each other, new forces of attraction and repulsion set in. The forces of attraction are between the nucleus of one atom and the electron cloud of the other and vice versa. The forces of repulsion are between two nuclei amongst themselves as well as between the electron clouds of the two atoms. (See Fig. 4.3). The net energy of the system is algebraic sum of attractive and repulsive forces.

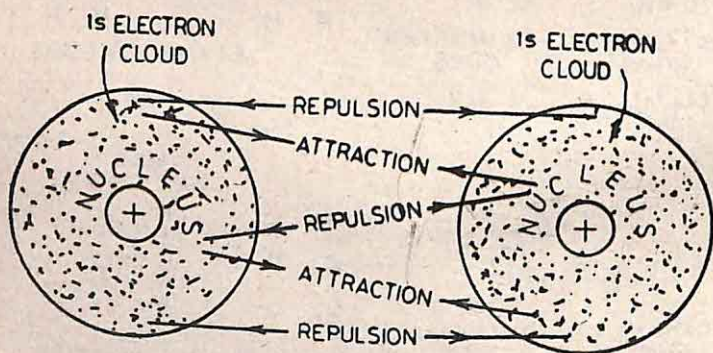


Fig. 4.3. Attractive and repulsive forces between two hydrogen atoms.

When the two hydrogen atoms are present at a large distance from each other, the potential energy of one atom is independent of the presence of the other. By convention, this energy is taken arbitrarily as zero. However, when the two atoms come closer together they begin to interact with each other (*i.e.*, the electronic

field due to one can influence that of the other) and energy changes begin to take place. This is due to the fact that when the atoms are sufficiently close, there is a possibility that the lone electron present in the $1s$ -orbital of one atom may move into the $1s$ -orbital of the other atom. But due to repulsion between the electrons, it is not likely that both the electrons can stay on the same atom. Actually, an exchange of electrons takes place from one atom to another. Thus, any electron may belong to any atom at any time.

When atomic orbitals of the two atoms start interacting (or overlapping) magnitude of attractive forces is greater than that of repulsive forces, and the energy of the system begins to decrease (see Fig. 4.4).

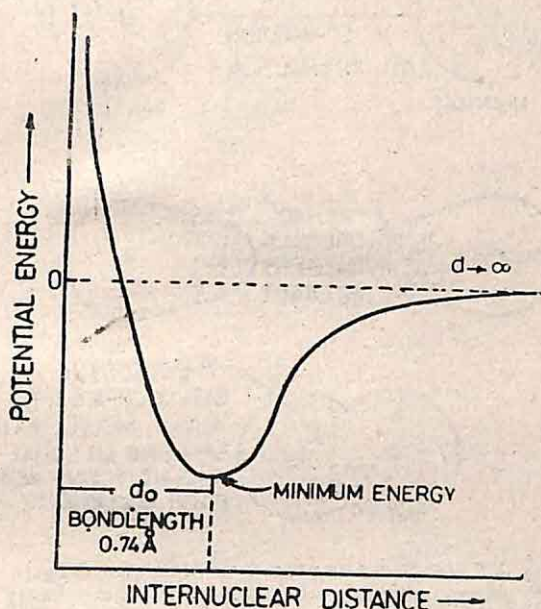


Fig. 4.4. Variation of potential energy as the two hydrogen atoms approach each other.

As the two atoms draw closer and closer their atomic orbitals overlap more and more and the energy of the system goes on decreasing. The decrease of energy continues till a certain minimum value is attained. If the atoms are brought still closer, the potential energy shows a sharp rise. This is due to the fact that the repulsive forces between the two nuclei at such a small internuclear distance becomes dominant. Since repulsion always causes increase in energy *i.e.*, the energy of the system rises as shown in the figure. The position of minimum energy at distance, d_0 between the nuclei of overlapping atoms corresponds to the formation of a stable covalent bond between the two hydrogen atoms. Moreover, the position of

minimum energy also corresponds to the minimum distance upto which the two nuclei can be brought together before the repulsive forces between them become dominant. Evidently, this corresponds to the bond length (*i.e.*, the distance between the nuclei of the two atoms constituting a chemical bond).

It may be pointed here that as the two atomic orbitals of hydrogen atoms overlap each other to form a covalent bond the two atomic orbitals actually merge together forming a new orbital called molecular orbital (*see* Fig. 4.5). Thus, this molecular orbital contains a pair of electrons.

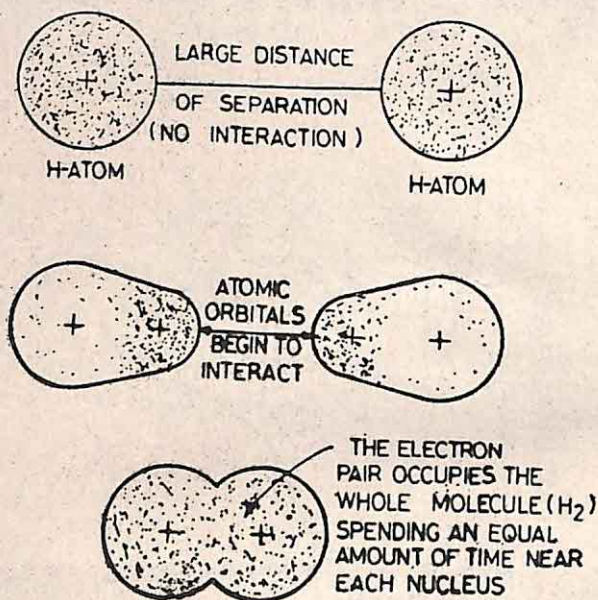


Fig. 4.5. (a) Separate atomic orbitals of hydrogen. (b) Atomic orbitals approach each other closely enough to begin to act upon each other. (c) Distribution of charge within the molecular orbital of a hydrogen molecule. The electron pair occupies the whole molecule spending an equal amount of time near each nucleus.

Let us now consider as to why helium (At. No. 2) does not form He₂ molecule. Unlike hydrogen, helium atom has got only a completely filled 1s-orbital. This completely filled orbital cannot overlap the completely filled 1s-orbital of another helium atom since it would go against the Pauli exclusion principle. The formation of helium molecule is also not feasible energetically. When two helium atoms approach near each other, the repulsive forces are stronger than the attractive forces and hence bond formation is not possible since net repulsive forces encountered leads to increase

in total energy of the system. Therefore, helium atoms cannot form bonds between them and exist merely as monoatomic gas.

4.8. SIGMA AND PIE BOND

As already learnt, a covalent bond is formed by overlapping (or coupling) of electrons with opposite spins belonging to the outer orbital of the two atoms involved. This process of overlapping is accompanied by the release of energy. It is evident that if overlapping is large, the energy released would be more and the resulting bond would be stronger since more energy would be needed to separate the bonded atoms. The extent of overlapping is determined by the nature of the atomic orbitals involved as well as the way in which they overlap each other. Depending upon these factors covalent bonds are classified into two types viz. sigma and pie bonds.

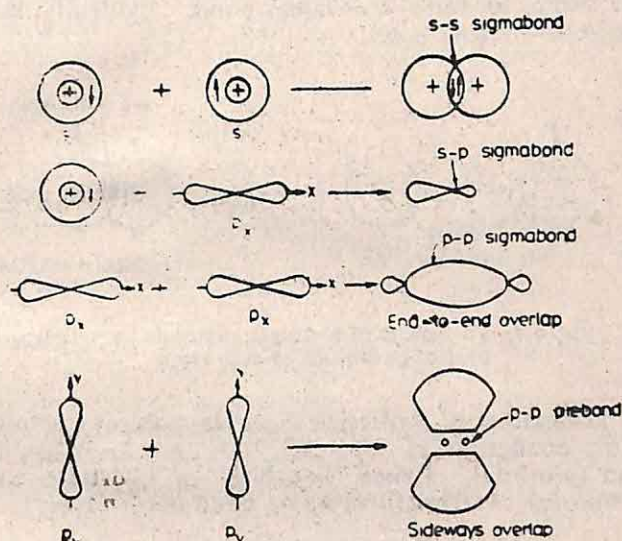


Fig. 4.6. Sigma and pie-bond formation.

(1) **Sigma (σ) bond.** When a bond is formed by overlapping of the orbitals along the internuclear axis (i.e., the line passing through the centers of nuclei of the two atoms) it is known as a sigma bond. Sigma bond is very strong bond. A sigma bond is formed (see Fig. 4.6) in case of :

- (i) s-s overlapping
- (ii) s-p overlapping, and
- (iii) p-p overlapping along the same axis.

The relative bond strength are of the order

$$p-p > s-p > s-s$$

$$3 \qquad 1.732 \qquad 1$$

(2) **Pie (π) bond.** When a bond is formed by the lateral or side-way overlapping of the orbitals, it is known as a pie bond. A π bond is a weak bond and is present in addition to the σ -bond in molecules containing double or tripple bond. A π -bond has no primary effect on the direction of the bond. It, however, shortens the internuclear distance. A pie bond is formed when $p-p$ orbitals overlap sideways. (see Fig. 4'6).

The formation of sigma and pie bonds is illustrated by the following examples.

1. **Formation of hydrogen molecule.** Hydrogen atom (At. No. 1 ; configuration $1s^1$) has one electron only in its $1s$ -orbital. It needs 1 more electron to complete this orbital. In the formation of hydrogen molecule, therefore, the $1s$ -orbital (half-filled) of one hydrogen atom overlaps with $1s$ -orbital (half-filled) of another hydrogen atom to form a covalent bond. Evidently, the bond in hydrogen is $s-s$ sigma bond.

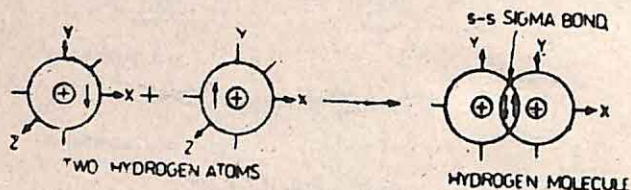


Fig. 4.7. Formation of hydrogen molecule by overlapping of $1s$ -orbitals of each atom.

2. **Formation of hydrogen fluoride molecule ;** Fluorine atom (At.No. 9 ; configuration $1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$) has only one half-filled $2p$ -orbital. Hence, $1s$ -orbital of hydrogen and $2p$ -orbital of fluorine overlaps form sigma bond of $s-p$ type.

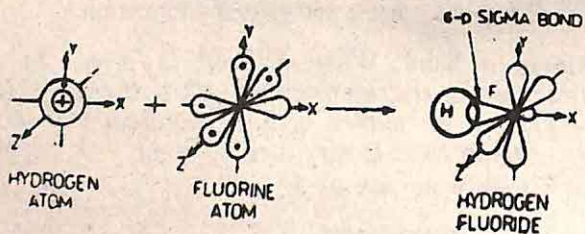


Fig. 4.8. Formation of hydrogen fluoride by overlapping of s -orbital of hydrogen atom and $2p$ -orbital of fluorine.

3. **Formation of fluorine molecule.** Fluorine molecule (F_2) is produced by $p-p$ overlapping between unpaired $2p$ -orbital of each

fluorine atom. Evidently, this involves a $p-p$ binding.

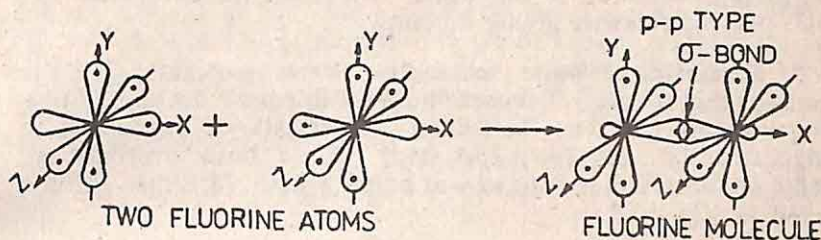


Fig. 4'9. Formation of fluorine molecule by overlapping of $2p$ -orbitals of two atom.

4. Formation of oxygen molecule. The electronic configuration of oxygen is $1s^2$; $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$. The $1s$ and $2s$ -orbitals are complete. But two $2p$ -orbitals are half-filled. Hence, the two half-filled $2p$ -orbitals of one oxygen atom overlap with the two corresponding half-filled $2p$ -orbitals of another oxygen atom to form O_2 molecule. This is represented in Fig. 4'10.

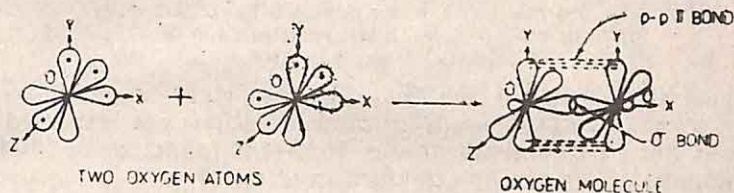


Fig. 4'10. Formation of oxygen molecule by overlapping of the two half-filled $2p$ -orbitals of each atom.

It will be seen that in one case, the $2p$ -orbitals overlap end-to-end giving σ -bond. In the other case, however, the $2p$ -orbitals overlap sidewise, resulting in a π -bond.

5. Formation of nitrogen molecule. The electronic configuration of nitrogen is $1s^2$; $2s^2$, $2p_x^1$, $2p_y^1$, $2p_z^1$. The $1s$ and $2s$ -orbitals are complete. But all the three $2p$ -orbitals are only half-filled. Hence, in the formation of N_2 molecule, the three half-filled $2p$ -orbitals of one nitrogen atom overlap with the three corresponding half-filled $2p$ -orbitals of another nitrogen atom. This is represented in Fig. 4'11.

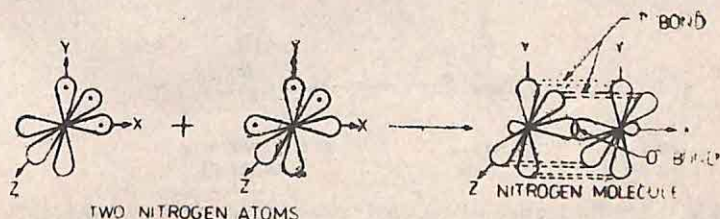


Fig. 4'11. Formation of nitrogen molecule by overlapping of the three half-filled $2p$ -orbitals of each atom.

It will be seen that in one case, the $2p$ -orbitals overlap end-to-end giving a σ -bond. In the other two cases, however, the $2p$ -orbitals overlap sidewise giving π -bonds.

6. Formation of water molecule. Water molecule (H_2O) is formed by the overlap between the half-filled $1s$ orbitals of two hydrogen atoms and two half-filled $2p$ -orbitals of oxygen atom (configuration $1s^2; 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$). Since both overlaps are co-axial, so, both bonds formed will be of sigma (σ) type. This is depicted in Fig. 4.12.

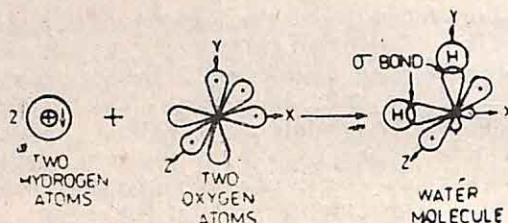


Fig. 4.12. Formation of water molecule by overlapping of $1s$ -orbitals of two hydrogen atom and two $2p$ -orbitals of oxygen atom.

Since the p -orbitals are mutually at right angles to one another, so, the two O-H bonds in water molecules are expected to be bent at 90° . However, the angle H-O-H is found to be 104.5° rather than 90° . This can be explained in terms of greater electronegativity of oxygen as compared to hydrogen. Due to this difference in electronegativity the O-H group of bond becomes polar so that hydrogen atom acquires some positive charge, while oxygen atom acquires negative charge. The observed bond angle of 104.5° is due to strong repulsion between the two positively charged polarised hydrogen atoms.

7. Formation of ammonia molecule. Ammonia molecule is formed by the overlapping between the half-filled $1s$ -orbitals of three hydrogen atoms and three half-filled $2p$ -orbitals of nitrogen ($1s^2, 2s^2; 2p_x^1, 2p_y^1, 2p_z^1$). Since all the overlaps are co-axial, so, all the three N-H bonds are of sigma type.

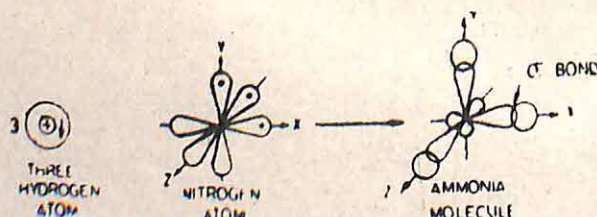


Fig. 4.13. Formation of ammonia molecule by overlapping of three $1s$ -orbitals of hydrogen atoms and three half-filled $2p$ -orbitals of nitrogen atom.

Since the three p -orbitals are inclined mutually at right angles to one another, so, the three N-H bonds are expected to be mutually inclined at 90° . But actually the bond angle is 107° rather than 90° . This can be explained in terms of repulsion between the polarised positive hydrogen atom (as in case of water) since electronegativity of nitrogen is greater than that of hydrogen.

4.9. HYBRIDISATION

The electronic configuration of beryllium, boron and carbon are:—

Be (At. No. 4)	$1s^2 ; 2s^2$
B (At. No. 5)	$1s^2 ; 2s^2, 2p_x^1$
C (At. No. 6)	$1s^2 ; 2s^2, 2p_x^1, 2p_y^1$

So, in terms of unpaired electron pairs concept of the orbital theory, beryllium would be expected to behave as an inert gas since it has no half-filled orbital. Boron, which has only one half-filled, $2p_x$ orbital, should behave as a monovalent element and form compounds like BeH and BeF. Carbon which has only two half-filled, $2p_x^1, 2p_y^1$ orbitals, should behave as a divalent element and form compounds like CH_2 and CCl_2 . But, actually this is not the case. Beryllium, unlike inert gases, forms compounds like BeF_2 and BeH_2 , in which it is bivalent. Boron forms compounds like BCl_3 and BH_3 , in which it is trivalent carbon forms over a million compounds like $\text{CH}_4, \text{CCl}_4$, in which it is invariably tetravalent.

In order to explain these anomalies, Linus Pauling (1931) introduced a new concept hybridisation. *The term called hybridisation may be defined as the mixing or redistribution of one or more orbitals of the outermost energy level (valency shell) of an atom to give new orbitals of equivalent energy.* The new orbitals thus formed are called "*hybrid orbitals*".

1. Hybridisation in beryllium. The electronic configuration of beryllium is $1s^2 ; 2s^2$. During bond formation say with fluorine, energy is released. This energy promotes one of the $2s$ -electrons into the empty $2p$ -orbitals. Thus, an excited beryllium atom possesses two half-filled $2s$ - and $2p$ -orbitals and hence beryllium is able to form compounds like BeF_2 . However, $2s$ - and $2p$ -orbitals have different energies and hence the two bonds in BeF_2 are expected to have different strength. But actually the two Be-F bonds possess

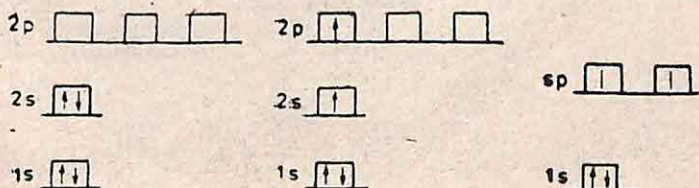


Fig. 4.15. Beryllium atom in (a) ground state (b) excited state, (c) hybridised state.

equal bond strength. This means that sp -hybridisation takes place in which $2s$ - and $2p$ half-filled orbitals have redistributed to form two colinear sp -hybrid orbitals of the same shape and strength. The large lobes of the two sp -orbitals protrude (Fig. 4.15) along the axis farther than the corresponding s - and p -orbitals. Consequently, a hybrid sp -orbital is able to form a stronger bond, by overlap with another orbital of another atom than either s - or p -orbitals alone.

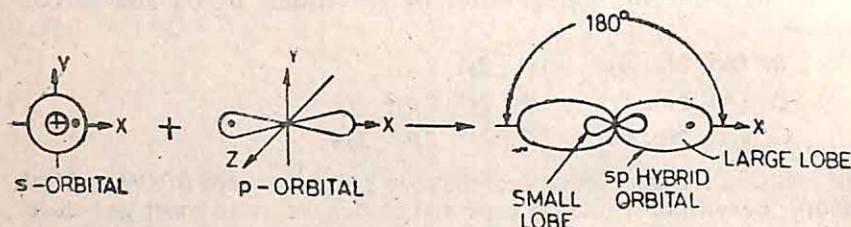


Fig. 4.16. Formation of two sp -hybrid orbitals.

It is now very easy to visualise the formation of beryllium fluoride (BeF_2) molecule. The electronic configuration of fluorine is $1s^2, 2s^2; 2p_x^2, 2p_y^2, 2p_z^1$. One of the p -orbitals is only half-filled. The half-filled orbitals of each fluorine atom overlap with one of the half-filled sp -hybrid orbitals of the beryllium atom to form two σ -bonds as illustrated in Fig. 4.16.

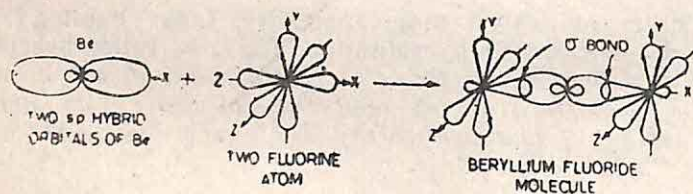


Fig. 4.17. Formation of beryllium fluoride molecules by the overlapping of the half-filled $2p$ -orbital of fluorine and sp -hybrid orbitals of beryllium atoms.

2. Hybridisation in boron. The electronic configuration of boron is $1s^2; 2s^2, 2p_x^1$. During bond formation, say with fluorine, energy is released. This energy promotes one of the $2s$ -

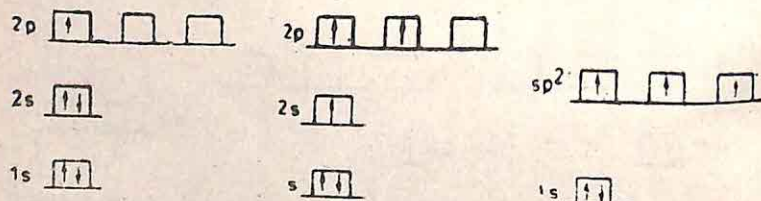


Fig. 4.18. Boron atom in (a) ground state, (b) excited state, (c) hybridised state.

electrons into one of the vacant $2p$ -orbitals. Thus, an excited boron atom possesses one $2s$ -orbital and two $2p$ -orbitals, which are half-filled. These three orbitals hybridise to give three sp^2 hybrid orbitals which are co-planar and directed at angles of 120° to each other (see Fig. 4.19). Like sp - hybrid orbitals, the sp^2 hybrid orbitals are able to form stronger bonds than s - and p -orbitals alone because, on account of their size they can overlap more effectively with other orbitals.

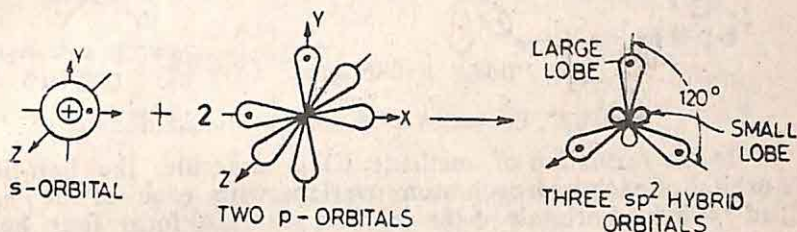


Fig. 4.19. Formation of three sp^2 hybrid orbitals.

In the formation of boron trifluoride, BF_3 , molecule the half-filled p -orbitals of each fluorine atom ($1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$) overlap with the half-filled sp^2 hybrid orbitals of the boron atom to form 3 σ -bonds as shown in Fig. 4.20.

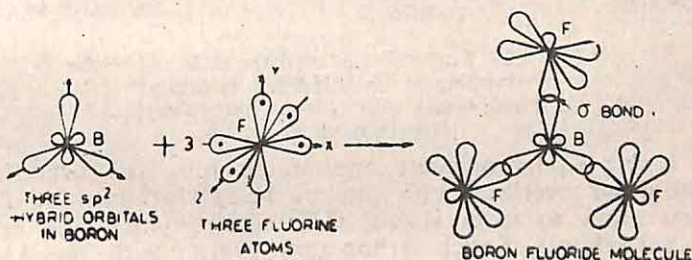


Fig. 4.20. Formation of boron trifluoride molecule.

3. Hybridisation in carbon. The electronic configuration of carbon atom is $1s^2, 2s^2, 2p_x^1, 2p_y^1$. When reacting atom, say, of hydrogen, approach to form covalent bonds, the energy is released

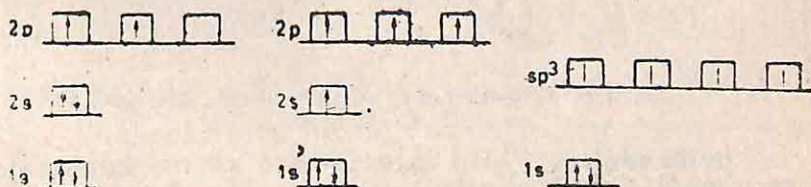


Fig. 4.21. Carbon atom in (a) ground state, (b) excited state, (c) hybridised state.

which promotes one of the $2s$ -electrons to one of the vacant $2p$ -orbitals which are half-filled. These four orbitals hybridise to give four sp^3 hybrid orbitals each directed towards the corners of a tetrahedron. The bond angles are of $109^\circ 28'$. This is shown pictorially in Fig. 4.22.

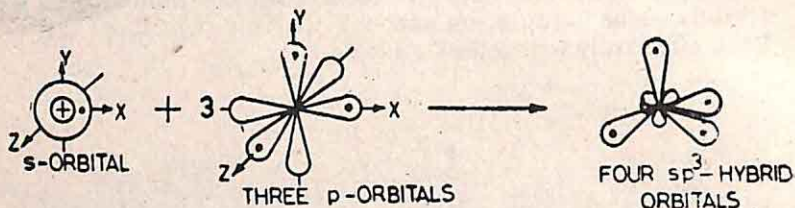


Fig. 4.22. Formation of four sp^3 hybrid orbitals.

In the formation of methane, CH_4 , molecule, the half-filled $1s$ -orbital of each hydrogen atom overlaps with each of the half-filled sp^3 hybrid orbitals of the carbon atom to form four bonds as shown in Fig. 4.23.

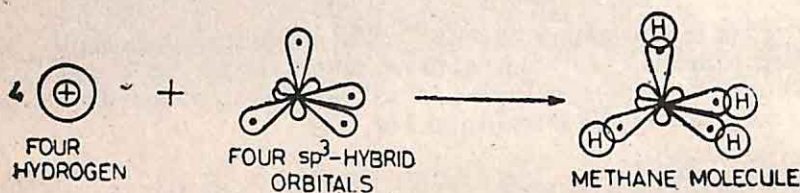


Fig. 4.23. Formation of methane molecule by the overlapping of the half-filled $1s$ -orbitals of 4 hydrogen atoms with the four sp^3 -hybrid orbitals of carbon atom.

In the (C_2H_6) molecule, one of the four sp^3 orbitals of one carbon atom overlaps with one of the sp^3 orbitals of the other carbon atom to form strong C-C sigma bond. The remaining three sp^3 orbitals of each carbon atom overlap with the $1s$ -orbitals of hydrogen atom to form C-H sigma bonds.

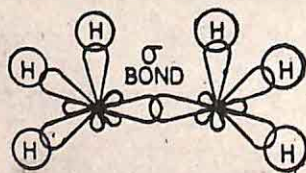


Fig. 4.24. Formation of an ethane molecule. The bond angle H-C-H is $109^\circ 28'$.

In the ethylene (C_2H_4) molecule each of the carbon atoms form bonds through sp^2 -hybrid orbitals. Two of the sp^2 orbitals of each carbon atom form σ -bonds with the $1s$ -orbitals of hydrogen

atoms. The remaining sp^2 orbital on each carbon atom forms a σ -bond between the carbon atoms. The two carbon atoms and four hydrogen atoms are all in the same plane and the bond angles are 120° (see Fig. 4.25). At right angles to this plane there is one unchanged $2p$ -orbital of each carbon atom; and the two $2p$ -orbitals, one on each carbon atom, overlap sideways to form a π -bond between the two carbon atoms. The double bond between the carbon atoms, therefore, consists of σ -bond and a π -bond.

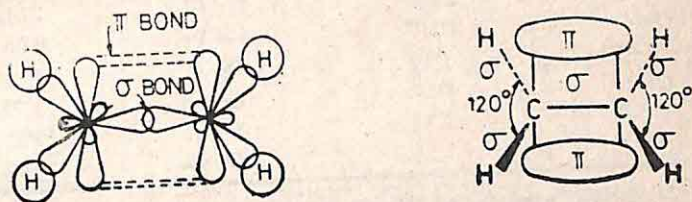


Fig. 4.25. Formation of an ethylene molecule. Four σ -bonds between carbon and hydrogen atom. One σ -bond and one π -bond between carbon atom.

In the acetylene (C_2H_4) molecule, hybridisation of one $2s$ - and one $2p$ -carbon orbitals leads to the formation of two collinear sp -hybrid orbitals. One of the sp -orbitals of carbon atom forms σ -bond with $1s$ -orbital of hydrogen atom. The remaining one sp -orbital of each carbon atom forms a σ -bond between the carbon atoms. The two carbon and two hydrogen atoms are all collinear (see Fig. 4.26).

At right angles to this line are two unchanged $2p$ -orbitals of each carbon atom and these interact to form two π -bonds in plane at right angles to each other. The triple bond between the carbon atom, therefore, consists of a σ -bond and two π -bonds.

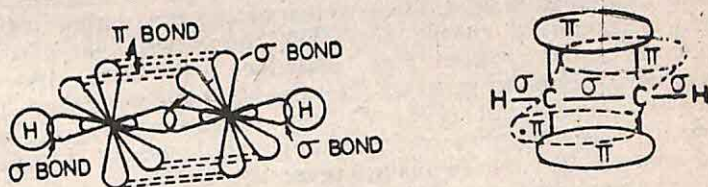


Fig. 4.26. Formation of acetylene molecule. Two σ -bonds between carbon and hydrogen atoms. One σ -bond and two π -bonds (in planes at right angles to each other) between carbon atoms.

4.10. IMPORTANT CHARACTERISTICS OF BOND

1. **Bond length.** Atoms in bond formation cannot come closer to each other than a certain equilibrium distance since in that case the potential energy of the system would tend to increase. The equilibrium distance between the centres of nuclei of two bonded atoms is known as the bond length or bond distance. It is expressed in

Angstrom units (\AA). The bond lengths have been determined in the case of crystals by X-ray diffraction method and in case of gases by spectroscopy. The actual bond length between two atoms depends upon the nature of the atoms and the nature of bond between them. Some of average values obtained are given below :

Bond	Bond length (\AA)	Bond	Bond length (\AA)
H—H	0.74	C \equiv C	1.20
N—N	1.094	H—Cl	1.27
O—O	1.207	H—Br	0.78
Cl—Cl	1.99	H—C	1.00
C—C	1.54	C—Cl	1.77
C=C	1.33	O—H	0.96
		C—O	1.42

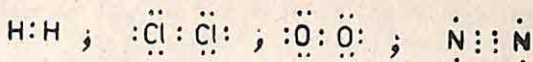
2. Bond energy or Bond strength. The process of bond formation is always accompanied by release of energy and the bonded state represents a state of lower energy than the individual atoms. Consequently, an equivalent amount of energy is required to break a chemical bond. For example, in the breaking of 1 mole of hydrogen atoms 432.2 kJ of energy is required. *Bond strength or bond dissociation energy is defined as the energy required to break a bond and separate the bonded atoms in the gaseous state.* It is expressed in kJ mol^{-1} .

The bond energy of a diatomic molecule indicates the stability of the bond. Greater the bond energy, greater is its stability. Bond energy of $\text{N}\equiv\text{N}$ is $941.4 \text{ kJ mol}^{-1}$ and that of $\text{O}=\text{O}$ is $401.7 \text{ kJ mol}^{-1}$. Hence, $\text{N}\equiv\text{N}$ bond is more stable than $\text{O}=\text{O}$ bond. In other word, nitrogen molecule is more stable than oxygen molecule. Consequently, nitrogen is found to be much less reactive than oxygen. It may be pointed here that the bond dissociation energy has a specific value for a given bond. When a certain bond is present in molecules of different substances, the actual values of bond dissociation energy for that bond will vary, from one compound to the other. For instance, the bond dissociation energy of O—H bond in water (H—O—H) is different than that in case of methyl alcohol ($\text{CH}_3\text{—O—H}$). Consequently, the general values of bond energies refer to only the average values. The bond energies of some bonds are given below :

Bond	Bond Energy (kJ mol^{-1})	Bond	Bond Energy (kJ mol^{-1})
H—H	432.2	C—H	414.4
H—Cl	432.6	C—C	341.4
O—H	461.2	C=C	611.3
N—H	388.7	C \equiv C	803.7
Cl—Cl	242.5	C—Cl	326.4
O=O	146.0	C—N	341.4
C—O	341.0	N—N	160.7
C=O	723.8	N=N	408.4
C \equiv O	1071.0	N \equiv N	1941.4

4.11. POLAR CHARACTER OF COVALENT BONDS

A covalent bond between an atom A and an atom B involves sharing of electrons and is represented as $A : B$. In a covalent bond between like atoms, the shared electron pair lies exactly in the centre of the two combining atoms and consequently it may be regarded as a true covalent bond *e.g.* non-polar bond.



On the other hand, in a covalent bond between unlike atoms the pair of shared electrons will not necessarily be shared equally by both atoms. Thus, in a bond $A-B$, if the atom B has a stronger attraction for the electrons than A, the shared pair will be attracted towards B and away from A. Any permanent displacement of electrons of this kind in a covalent bond will give the bond some ionic or polar character and the actual bond will have to be represented as



In terms of molecular orbitals, the polar character of a covalent bond can be represented by the shape of the orbital as indicated in Fig. 4.27.

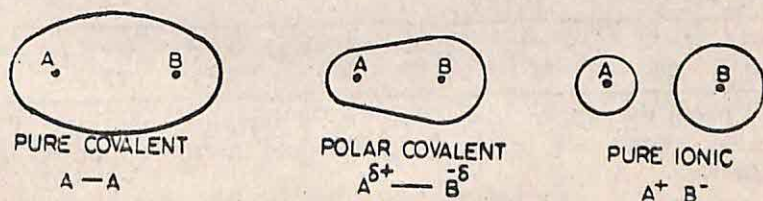


Fig. 4.27. General shape of orbitals representing transition from pure covalent to pure ionic bonding.

The extent of the ionic character in a covalent bond depends on the relative attraction for electrons of the bonded atoms. *The ability of an atom to attract the shared electron pair towards itself is known as the "electronegativity" of the atom.* The numerical value of electronegativities for some elements are summarised in Table 4.1.

Table 4.1. Electronegativity values (Pauling).

H						
2.1						
Li	Be	B	C	N	O	F
1.0	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca			As	Se	Br
0.8	1.0			2.0	2.4	2.8
Rb	Sr			Sb	Te	I
0.8	1.0			1.9	2.1	2.5
Cs	Ba			Bi	Po	At
0.7	0.9			1.9	2.0	2.2

The extent of ionic character or polarity of the covalent bond depends on the difference in the electronegativities of the two atoms involved in the bond formation. Thus, the polarity of the bond in the hydrogen halides increases in the order HI, HBr, HCl and HF corresponding to an increase in electronegativity of halogen I (2.5), Br (2.8), Cl (3.0), and F (4.0). Prof. Linus Pauling calculated numerical relationship between percentage ionic character of a covalent bond and the difference in the electronegativities of the involved atoms. His findings are given in Table 4.2.

Table 4.2. Electronegativity difference and ionic character.

Electronegativity difference	0.1	0.3	0.4	0.5	0.9	1.1	1.4	1.5	1.9	3.0	3.3
Percent ionic character	0.5	3	4	11	19	25	39	43	60	90	100

On this basis, the percentages of ionic character in typical bonds are given as follows.

C—I;	C—Br;	C—H;	C—Cl;	N—H;	O—H;	C—E;	F—H
0%	3%	4%	11%	19%	39%	43%	60%

From the above discussion, it is obvious that most of the covalent bonds are partially polar and partially non-polar in character.

4.12. DIPOLE MOMENT

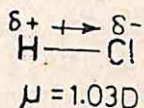
Molecules are composed of positively charged nuclei and an equivalent amount of negatively charged electron cloud around them. In most of the molecules, the centre of positive and negative charges do not coincide and as a result there is present in such molecules, two oppositely charged poles separated by a definite distance. Such a molecule is said to possess a dipole. *The product of the net positive or negative charge (e) multiplied by the distance (d) between the centres of positive and negative electricity in a molecule is called its dipole moment (μ).* Mathematically,

$$\text{Dipole moment } (\mu) = \text{net charge } (e) \times \text{distance } (d)$$

Since charge (e) is of the order of 10^{-10} esu and distance (d) is of the order of 10^{-8} cm, the value of dipole moment (μ) will be of the order of 10^{-18} esu-cm and this unit is known as Debye unit (D). Thus, $D = 1 \times 10^{-18}$ esu-cm.

Dipole moment is a vector quantity and is often represented by a little arrow with a tail sitting at the positive centre and head pointing towards the negative centre.

The value of dipole moment of a substance can, in simple cases, be used to estimate the ionic character of a bond. The dipole moment of HCl, for example, is 1.03D. If the bond in the molecule



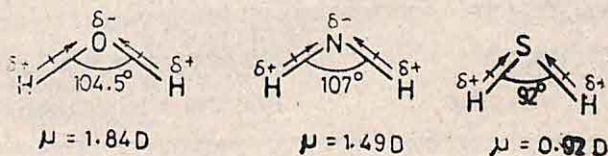
were fully ionic the expected dipole moment would be equal to the charge on the electron multiplied by bond distance *i.e.*,

$$4.802 \times 10^{-10} \text{ esu} \times 1.27 \times 10^{-8} \text{ cm} = 6.07 \times 10^{-18} \text{ esu-cm.} \\ = 6.07 \text{ D.}$$

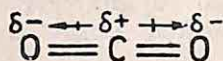
The ionic character of the H—Cl bond may, therefore, be taken as $(1.03/6.07) \times 100$ percent, *i.e.*, approximately 17 percent. This result is in good agreement with that obtained from the electronegativity values of hydrogen and chlorine.

In case of molecules containing more than two atoms, the magnitude of dipole moment depends not only on the values of individual dipole moments of various bonds, but also on the arrangement of these polar bonds in space. Thus, dipole moment of water (1.84 D) is the resultant of the individual values of two O—H groups having a bond angle of 104.5° . Similarly, the dipole moments of NH_3 and H_2S are 1.49 D and 0.92D respectively.

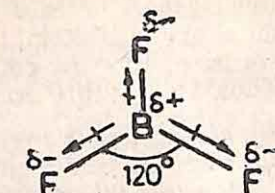
The resultant molecular dipole moments of these compounds, thus, indicates molecular non-symmetry, *i.e.*, all atoms in their molecule cannot lie in one straight line.



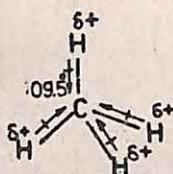
On the other hand, substances like CO_2 , BF_3 , CH_4 , CCl_4 , etc. having zero dipole moment indicates a symmetry in their molecule. In these molecules individual dipole moments cancel out each other and the net resultant is zero.



RESULTANT $\mu = 0$
(SYMMETRICAL LINEAR)

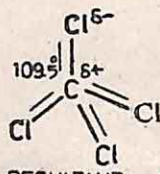


RESULTANT $\mu = 0$
(SYMMETRICAL FLAT)



RESULTANT $\mu = 0$
(SYMMETRICAL TETRAHEDRON)

(Four hydrogen atoms are attached to the four corners of a regular tetrahedron with carbon atom at its centre).



RESULTANT $\mu = 0$
(SYMMETRICAL TETRAHEDRON)

(Four chlorine atoms are attached to the four corners of a regular tetrahedron with carbon atom at its centre).

From the above discussions, we can sum up that for a polyatomic molecule to have a net dipole moment it should not only contain polar bonds but it must also have an unsymmetrical structure.

The dipole moments of some common molecules are given below :

Substance	Dipole moment (D)
$H_2, N_2, O_2, Cl_2, Br_2$	0 each
CH_4, CCl_4, CO_2, BF_3	0 each
$HF; HCl; HBr; HI$	1.91 ; 1.03 ; 0.78, 0.38 respectively
$H_2O; SO_2; NH_3; H_2S$	1.84, 1.60, 1.49, 0.92 respectively

Example 4.1. The internuclear separation in a potassium chloride molecule in the vapour state is 2.67 \AA . Assuming complete transfer of electron from the potassium atom to the chlorine atom, calculate the dipole moment of KCl molecule. (Electronic charge $= 4.802 \times 10^{-10} \text{ esu}$).

$$\begin{aligned}
 \text{Dipole moment (u)} &= \text{Charge} \times \text{distance of separation} \\
 &= 4.802 \times 10^{-10} \text{ esu} \times 2.67 \text{ \AA} \\
 &= 4.802 \times 10^{-10} \text{ esu} \times 2.67 \times 10^{-8} \text{ cm.} \\
 &= 12.81 \times 10^{-18} \text{ esu} \times \text{cm.} \\
 &= 12.81 \text{ D.}
 \end{aligned}$$

Example 4.2. The dipole moment of HCl is 1.30D and bond distance is 1.275 Å. Estimate the ionic character of the bond (Electric charge = 4.8×10^{-10} esu).

If we consider the molecule to be composed of two separate ions (i.e., 100% ionic character), then the dipole moment would be

$$\begin{aligned}
 &= 4.8 \times 10^{-10} \text{ esu} \times 1.275 \times 10^{-8} \text{ cm.} \\
 &= 6.1 \times 10^{-18} \text{ esu} \times \text{cm.} \\
 &= 6.1 \text{ D.}
 \end{aligned}$$

Hence, % of ionic character

$$= \frac{1.03 \text{ D}}{6.1 \text{ D}} \times 100 = 17\%.$$

4.13. PROPERTIES OF COVALENT COMPOUNDS

1. Directional nature. As the covalent bonds are formed by the overlapping of the atomic orbitals, and the molecular orbitals thus formed are more concentrated along certain directions, consequently, covalent bond is directional.

2. State of existence. Since these compounds are formed by sharing of electrons between the individual atoms, so they exist as molecules. They are generally gases or liquids. On the other hand, covalent compounds in solid form are either amorphous or molecular crystals having weak intermolecular forces.

3. Low melting and boiling points. Due to the presence of weak intermolecular forces covalent compounds, generally, have low melting and boiling points.

4. Non-conducting nature. Since these compounds exist as molecules rather than ions, they do not conduct electricity in fused or dissolved state.

5. Solubility. These compounds are, generally, slightly soluble in water but freely soluble in organic solvents.

6. Isomerism. In certain cases they can exhibit space isomerism and stereoisomerism since covalent compounds involve definite bond angles.

7. Non-ionic reactions. The reactions involving covalent compounds usually take place between molecules rather than ions.

4.14. GEOMETRY OF COVALENT MOLECULES

In the formation of simple covalent molecules, there is one central atom which forms covalent bonds with other atoms. For

example, in the formation of molecule of water (H_2O), ammonia (NH_3), and methane (CH_4), the central atom is O, N, and C respectively and these form two, three and four covalent bonds respectively with hydrogen atoms.

We also know that in the formation of covalent bonds, orbitals get occupied by electrons in pair. Consequently, a central atom forming more than one covalent bonds will be surrounded by more than one such orbitals. Moreover, electrons experience electrostatic repulsion from one another, so, orbitals containing electrons also experience electrostatic repulsion. The orbitals, therefore, tend to keep apart from one another as far as possible so that they may experience minimum electrostatic repulsion. This gives minimum energy (or maximum stability) to the molecule.

This forms the basis of **Valence Shell Electron Pair Repulsion (VSEPR) model**. According to this model *"for maximum stability of a molecule the orbitals occupied by electrons in the valence shell of the central atom must stay in space as far as possible. Moreover, the orbital of a non-bonding (or lone pair) valency shell electrons occupies more space than the orbital having a bonding pair of valence electrons."* This is because a non-bonding pair of electron is under the influence of only one nucleus; while the bonding pair of electron is attracted by two nuclei. Thus, non-bonding pair of electrons, under the attractive influence of one nuclei only, repels the other pair of electrons to a greater extent.

VSEPR model predicts the shape or geometry of different molecules in a very simple way. Based on this model geometry of molecules can be regular or irregular.

(1) *If the central atom is surrounded only by orbitals containing shared or bonded pairs of electrons and there is no orbital containing lone pair in the valency shell, the molecule has a "regular geometry".*

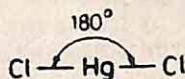
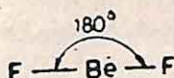
(2) *If the central atom is surrounded by orbitals containing shared pairs of electrons together with one or more lone electrons pairs in the valence shell, the molecule do not pertain to any regular geometry. The molecule in such a case is said to have "irregular geometry".*

Based on the above facts, let us try to predict the geometry of some of the simple molecules.

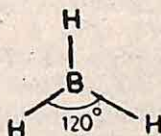
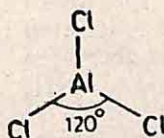
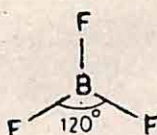
(A) Geometry of molecules containing only bonding pairs of electrons.

1. *Molecules in which central atom is surrounded by two bonding pairs of electrons.* A molecule having only two bonding pairs of electrons around the central atom (such as BeF_2 , HgCl_2) would always have a linear arrangement of atoms because this arrangement puts the two pairs of valence shell electrons as far apart from each other as possible in order to get maximum stability. Consequently, the bond angles $\text{F}-\text{Be}-\text{F}$ and $\text{Cl}-\text{Hg}-\text{Cl}$

is equal to 180° , as shown below :



2. *Molecules in which central atom is surrounded by three bonding pairs of electrons.* A molecule having only three bonding pairs of electrons around the central atom (such as BH_3 , BF_3 , BCl_3 , AlCl_3) would always have a plane triangular arrangement of atoms because this puts the three pairs of valence shell electrons as far apart from one another as possible in order to get maximum stability. Thus, the bond angle $\text{H}-\text{B}-\text{H}$, etc., is 120° as shown below :



3. *Molecules in which central atom is surrounded by four bonding pairs of electrons :* A molecule having only four bonding pairs of electrons around central atom (such as CH_4 , CCl_4) would always have tetrahedral geometry (i.e., four electron pairs are placed at the vertices of a tetrahedron and central atom is at the centre) of atoms because this puts the four pairs of valency shell electrons as far apart from one another as possible in order to get maximum stability. Thus, bond angle $\text{H}-\text{C}-\text{H}$ in CH_4 is $109^\circ-28'$, as shown in Fig. 4.28.

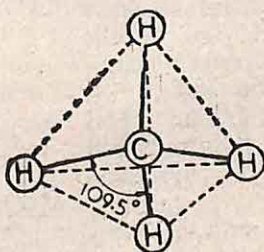
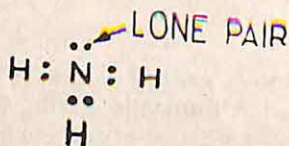


Fig. 4.28. Tetrahedral structure of methane molecule.

B. Geometry of molecules containing bonding pairs as well as lone pairs of electrons :

1. *Molecule in which central atom is surrounded by three*

bonding pairs and one lone pair of electrons. For example, let us consider the case of ammonia in which the central atom, nitrogen, is surrounded by four pairs of electrons, three of which are bonding while the fourth is lone pair.



According to VSPER theory, the orbitals should be tetrahedral to have minimum repulsion. However, the orbital containing a lone pair occupies more space and repels the other three bonding orbitals to a greater extent. The molecule, therefore, gets a little distorted and the bond angle, $\text{H}-\text{N}-\text{H}$ decreases from 109° to 107° . The shape of NH_3 molecule is thus pyramidal in which H atom lies at the centre and three H atoms form the base; and the lone pair of electrons forms the apex of the pyramid, as shown in Fig. 4.29.

distribution of these four

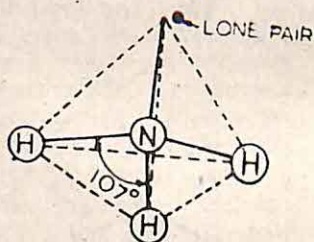
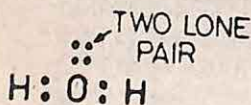


Fig. 4.29. Pyramidal structure of ammonia molecule.

2. *Molecule in which the central atom is surrounded by two bonding pairs and two lone pairs of electrons.* For example, let us consider the case of water in which the central O atom is surrounded by four pairs of electrons, two of which are bonding pairs while the rest two are lone pairs.



According to VSPER theory, the distribution of these four orbitals should be tetrahedral to have minimum repulsion. However, the orbitals containing lone pairs occupy more space and repel the other two bonding orbitals to greater extent. The molecule, therefore, gets distorted and the bond angle $\text{H}-\text{O}-\text{H}$ decreases from 109.5° to 104.5° . It may be recalled that the force of repulsion between two lone pairs of electrons amongst themselves is more than the force of repulsion between two bonding electron pairs, so, there is greater distortion in H_2O molecule than in ammonia. Consequently, the bond angle $\text{H}-\text{O}-\text{H}$, in water is smaller than the bond angle $\text{H}-\text{N}-\text{H}$. The molecule of water is also described as V-shaped structure (see Fig. 4.30).

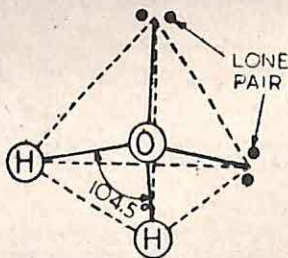
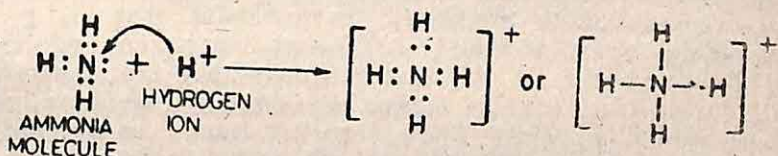


Fig. 4.30. V- shaped molecule of water.

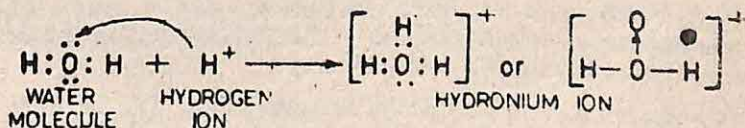
4.15. DATIVE OR CO-ORDINATE COVALENT BOND

Sometimes the shared pair of electrons of a covalent bond may also be formed by one of the two bonded atom. In such a case the bond is called a **dative bond** or **co-ordinate covalent bond**. The atom providing the two electrons (called, *lone pair*) to make up the dative bond is known as the *donor*. The atom sharing the pair of electrons from the donor is known as the *acceptor*. It may be pointed that the formation of a co-ordinate covalent bond is possible only between an atom with an unshared pair of electrons in its valence shell and an atom or ion that needs a pair of electrons to acquire a stable electronic configuration. The chief difference between the co-ordinate bond and the covalent bond is in the mode of formation. Once established, they are indistinguishable. To distinguish co-ordinate bond from the covalent bond, the former is generally represented by an arrow pointing from the donor to the acceptor.

An example of co-ordinate covalent bond is provided by the ammonium ion, NH_4^+ . The bonds in the ammonia molecule itself are of the covalent type. One unshared pair of electrons of the nitrogen atom is available for use in bond formation, as indicated by the readiness with which ammonia will combine with a hydrogen ion to form the ammonium ion.



Because NH_3 is a neutral molecule, the union with a hydrogen ion (proton) gives a unit positive charge to the resulting ammonium ion. In a similar fashion, water molecule combines with hydrogen ion to form hydronium ions, $(\text{H}_3\text{O})^+$.



Some other examples of the formation of co-ordinate bonds are as follows :

orbitals should be tetrahedral to have minimum repulsion. However, the orbital containing a lone pair occupies more space and repels the other three bonding orbitals to a greater extent. The molecule, therefore, gets a little distorted and the bond angle, $\text{H}-\text{N}-\text{H}$ decreases from 109° to 107° . The shape of NH_3 molecule is thus pyramidal in which H atom lies at the centre and three H atoms form the base; and the lone pair of electrons forms the apex of the pyramid, as shown in Fig. 4.29.

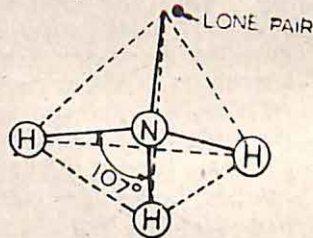
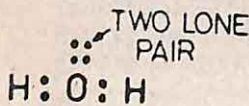


Fig. 4.29. Pyramidal structure of ammonia molecule.

2. *Molecule in which the central atom is surrounded by two bonding pairs and two lone pairs of electrons.* For example, let us consider the case of water in which the central O atom is surrounded by four pairs of electrons, two of which are bonding pairs while the rest two are lone pairs.



According to VSEPR theory, the distribution of these four orbitals should be tetrahedral to have minimum repulsion. However, the orbitals containing lone pairs occupy more space and repel the other two bonding orbitals to greater extent. The molecule, therefore, gets distorted and the bond angle $\text{H}-\text{O}-\text{H}$ decreases from 109.5° to 104.5° . It may be recalled that the force of repulsion between two lone pairs of electrons amongst themselves is more than the force of repulsion between two bonding electron pairs, so, there is greater distortion in H_2O molecule than in ammonia. Consequently, the bond angle $\text{H}-\text{O}-\text{H}$, in water is smaller than the bond angle $\text{H}-\text{N}-\text{H}$. The molecule of water is also described as V-shaped structure (see Fig. 4.30).

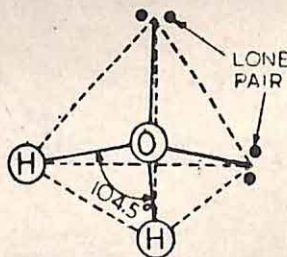
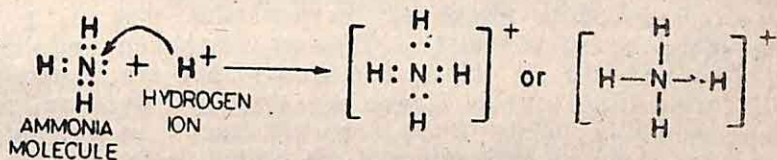


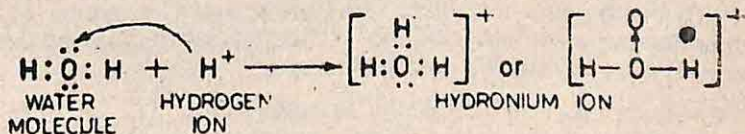
Fig. 4.30. V-shaped molecule of water.

of formation. Once established, they are indistinguishable. To distinguish co-ordinate bond from the covalent bond, the former is generally represented by an arrow pointing from the donor to the acceptor.

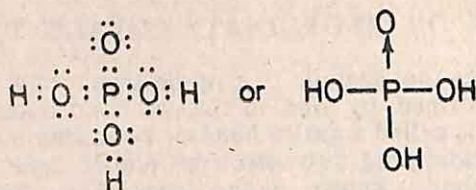
An example of co-ordinate covalent bond is provided by the ammonium ion, NH_4^+ . The bonds in the ammonia molecule itself are of the covalent type. One unshared pair of electrons of the nitrogen atom is available for use in bond formation, as indicated by the readiness with which ammonia will combine with a hydrogen ion to form the ammonium ion.



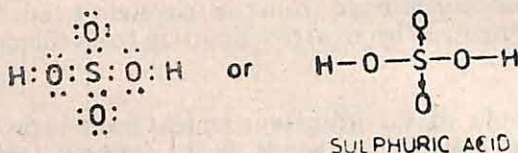
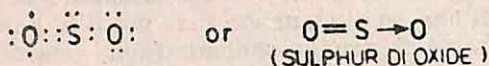
Because NH_3 is a neutral molecule, the union with a hydrogen ion (proton) gives a unit positive charge to the resulting ammonium ion. In a similar fashion, water molecule combines with hydrogen ion to form hydronium ions, $(\text{H}_3\text{O})^+$.



Some other examples of the formation of co-ordinate bonds are as follows :



Ortho phosphoric acid.



4.16. METALLIC BOND

With the exception of mercury (m.pt. 234K) and gallium (m.pt. 303K) all metals are solids at ordinary temperatures. They possess very distinctive properties. In particular, they are good electrical and thermal conductors. They are very opaque and have high reflecting power, *i.e.*, they are lustrous; they are, generally, hard, ductile (*i.e.*, can be drawn into sheets); they have high melting and boiling points. Such properties cannot be accounted for in terms of normal ionic or covalent bonding, so the idea of a special type of bond known as metallic bond is necessary.

The general picture of the state of affairs in the crystal of a metal can be understood by considering the following facts.

(i) *Metals, generally, have low ionisation energies being always less than 920 kJ mol⁻¹ (except mercury whose ionisation energy is 1003 kJ mol⁻¹). This implies that valency electrons in metals are weakly bound to the kernel*.*

(ii) *The number of valency electrons in metallic atoms is less than the number of valence orbitals. This implies that a number of valence orbitals in metallic atoms are empty.*

Consider the case of lithium (configuration 1s², 2s¹). It has only one valence electron. X-ray examination of a crystal of lithium shows that each lithium atom is surrounded by eight other lithium atom. So, it is not possible to visualize that one lithium

*By kernel is meant the nucleus plus electrons except those in the valency (outermost) shell.

atom can get bonded to eight other atoms through covalent bonds, since it contains only one valency electron. However, it has four valency orbitals (*viz.*, $2s$, $2p_x$, $2p_y$, $2p_z$). Hence, besides its own valency electron, the valency electrons of the neighbouring lithium atoms can also come quite close to its nucleus. In other words, the electrons from one atom can freely move in the vacant valence orbitals of another atom. Thus, the valency electrons of the metallic atoms do not belong to one atom in particular, and can freely move about from one kernel to another in crystal. The valency electrons of the metallic atoms are thus delocalized. They are, in effect, a common property of all atoms present in a metallic crystal.

Based on the above ideas, an **electron gas model for metallic crystals** have been given. According to it a *metallic crystal consists of an orderly assemblage of positive ions (kernels) immersed*

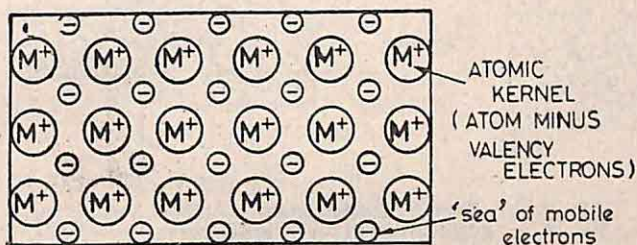


Fig. 4.30. Structure of metallic crystal.

in [a 'sea' of mobile electrons (see Fig. 4.30) ; and the force that binds a metal ion (kernel) to the number of electrons within its sphere of influence is known as metallic bond.

Explanation of properties of metals.

(i) **Electrical conductivity.** In a metal, the electrons are mobile and they are moving probably equally in all directions. However, when a potential difference is applied across a metal, the flow of electrons occur along the direction of electric field and electric current is carried from one point to another. This explains good conductivity of metals. On raising the temperature of a metal, the kinetic energy of positive kernels and consequently their vibrations is increased. This interferes with the directed flow of electrons through the metal crystal. As a result of this the resistance of a metal increases and its conductivity decreases with the rise in temperature.

(ii) **Thermal conductivity.** On heating a part of the metal, the mobile electrons in that region acquire high kinetic energy. These energised electrons move rapidly to the colder parts of the metal and in doing so some of their energy is transferred to these parts. As a result of this, temperature of these parts is also raised, and in this way, heat gets conducted throughout the metal.

(iii) *Metallic lustre.* When visible light falls on the surface of a metal, the surface electrons of the latter absorb the photons of incident light. But this absorbed light energy is immediately re-emitted in the form of electromagnetic radiations of same frequencies. Consequently, due to this momentary exchange of light energy, the metal surface exhibits a shining appearance.

(iv) *Malleability and ductility.* The valency electrons in a metallic bond are spread all over the crystal, more or less uniformly. So, the positive kernels in a crystal can be moved past one another with relative ease, provided their average inter-kernel distance are not changed. In other words, under the influence of an external

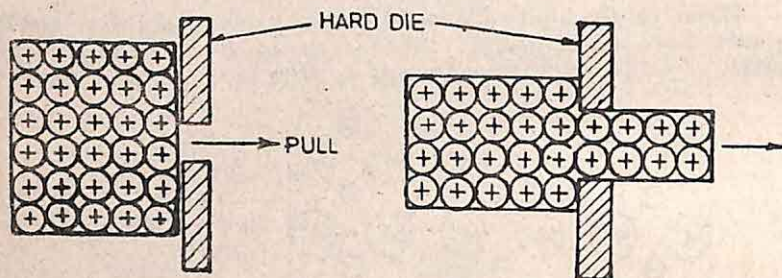


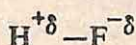
Fig. 4.31. Relative displacement of metal kernel on application of an external stress.

stress, the position of one group of kernels can be changed relative to the neighbouring groups of kernels, without changing their relative positions with respect to the surrounding sea of electrons (see Fig. 4.31). Thus, the non directional nature of the metallic bond is responsible for the high malleability and ductility of the metals.

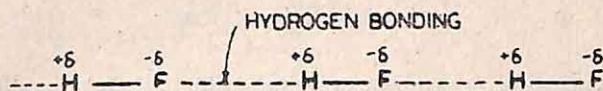
4.17. HYDROGEN BOND

Many compounds containing hydrogen attached to fluorine, nitrogen or oxygen, have been found to exhibit unexpected properties such as relatively high boiling points and high heat of vaporisation. An explanation sought for this has ultimately led to a new concept termed as hydrogen bond. *Hydrogen bond is an electrostatic attractive force which binds covalently bonded hydrogen atom of one molecule with an electronegative atom (such as fluorine) of another molecule of the same substance.*

Formation of hydrogen bond. When hydrogen is covalently bonded with strongly electronegative atoms (like F, N and O), the shared electron pair between the two atoms lie much more nearer the electronegative atom. This results in the development of a highly electropositive charge on the hydrogen atom with respect to the other atom. For example, hydrogen fluoride molecule can be represented as :



This positively charged hydrogen atom end attracts and is attracted by the negative end of the other molecule. Thus, two or more molecules may associate together to form clusters of molecules e.g.,



This electrostatic force of attraction (known as hydrogen bond) is represented by dotted lines, as shown above. It may be noted that hydrogen atom is bonded to electronegative atom, fluorine, by a covalent bond in one molecule and by hydrogen bond to the fluorine atom in the adjacent molecule. Consequently, hydrogen acts as a *bridge* between the two fluorine atoms.

Conditions for hydrogen bonding. For an effective hydrogen bond to be formed, the other atom bonded to hydrogen atom should be *small in size* and *highly electronegative*. Fluorine, nitrogen and oxygen are the only three elements* which possess these requisite characteristics for hydrogen bond formation.

Examples of hydrogen bond.

(1) **Hydrogen fluoride.** Pure hydrogen fluoride differs from the other hydrogen halides (*viz.*, HCl, HBr, and HI) because of its tendency to associate through hydrogen bonding. In the solid state hydrogen fluoride exists as zig-zag chains of molecules which extend the entire length of the crystal (Fig. 4.32). Each hydrogen atom lies closer to the more firmly attached covalently bonded fluorine atom.

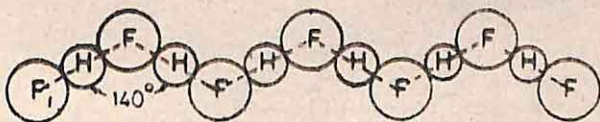


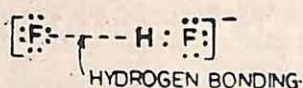
Fig. 4.32. Illustration showing associated nature of HF resulting from hydrogen bonding.

Vapour density measurement shows hydrogen fluoride gas to be a mixture of $(\text{HF})_2$ and $(\text{HF})_3$ at 299K. On heating progressively, the length of chain shortens. Thus, vapour density of hydrogen fluoride at 361K corresponds to the formula HF, *i.e.*, undissociated.

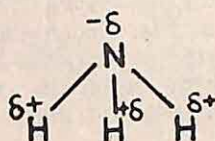
In aqueous solution, hydrogen fluoride ionises to yield, not the simple F^- ions, but the $(\text{FHF})^-$, in which also the hydrogen atom

*Chlorine has the same electronegativity as nitrogen, but the former does not form effective hydrogen bond because the size of chlorine atom is quite large and as a result its electrostatic interactions are weak.

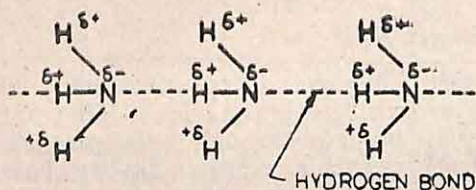
acts as a bridge between the two fluorine atoms, as shown below :



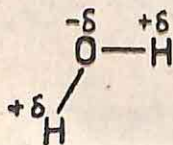
(2) **Ammonia.** Ammonia molecule is also a dipole, the nitrogen end carrying a negative charge and the hydrogen end carrying a positive charge, as shown below :



Ammonia also associates through hydrogen bonding to form big chains readily.



(3) **Water.** Water molecule is also a dipole, the oxygen end carrying a negative charge and the hydrogen end carrying a positive charge, as shown below :



Water also undergoes association through hydrogen bonding, as represented below :

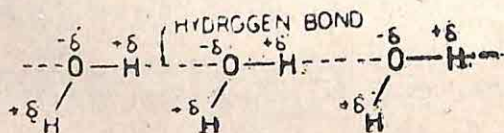


Fig. 4.33. Hydrogen bond causing association in water.

The presence of above eight membered ring in carboxylic acids has been confirmed by electron diffraction studies.

In aqueous solution, the molecules of a carboxylic acid link up with water molecules rather than forming dimers.

Consequences of hydrogen bonding. (i) Association. As already illustrated, the molecules linked by hydrogen bonds associate with one another to form associated units, each of which may contain 2 or more molecules.

(ii) Higher melting and boiling points. The presence of hydrogen bonding in these compounds is indicated by higher melting points, boiling points, heats of vaporisation and viscosities than shown by corresponding normal liquids. The abnormal

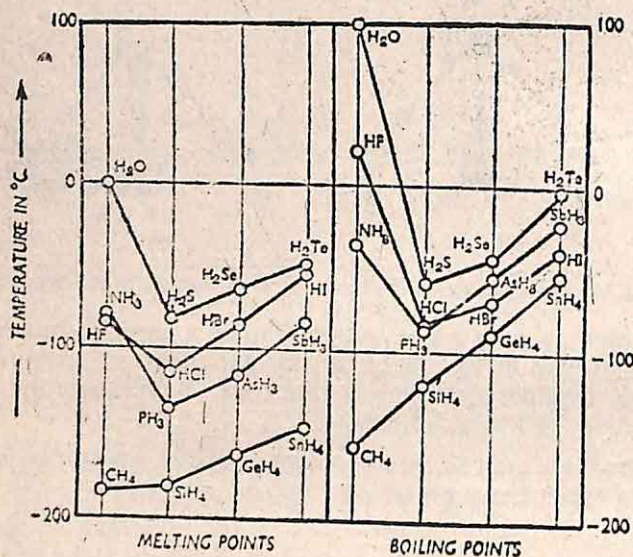


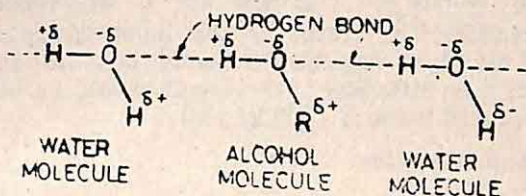
Fig. 4.35. The abnormal melting and boiling points of water, hydrogen fluoride and ammonia.

melting and boiling points of NH₃, H₂O and HF, due to association caused by the formation of hydrogen bonds, is shown in Fig. 4.35. The increased inter-molecular forces of attraction due to hydrogen bonding requires an increased amount of energy to separate the molecules. This consequently leads to abnormal high melting and boiling points.

For the same reasons, there is a marked difference between the boiling points of alcohols and the corresponding sulphur analogues (thiols) *e.g.*,

Boiling point	CH ₃ OH 337.5K	C ₂ H ₅ OH 351K	C ₃ H ₇ OH 370K	C ₄ H ₉ OH 390K
Boiling point	CH ₃ SH 278.8K	C ₂ H ₅ SH 310K	C ₃ H ₇ SH 340K	C ₄ H ₉ SH 370K

(iii) **Solubility.** Generally compounds which can form hydrogen bonds with the solvent molecules are soluble in such solvents. For examples, lower alcohols are soluble in water due to hydrogen bonding, which can exist between alcohol and water molecules.



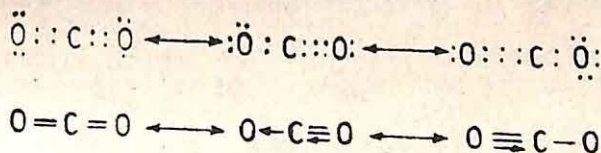
4.18. RESONANCE

It has been observed that the arrangement of electrons in molecules of a particular compound cannot be explained satisfactorily in terms of a single structure. For example, no single, simple structural formula, which can be written for carbon dioxide, accounts for all the known properties of carbon dioxide.

The actual electronic arrangement in a compound, which cannot be satisfactorily represented in one single structural formula using accepted symbols, is represented in terms of a new concept called **resonance**. According to this concept if a molecule can be assigned two or more reasonable electronic structures none of which alone is capable of explaining all the known properties of the compounds, the "real" structure is identical to neither, but is intermediate in character between these structures. The real structure is often called a *resonance hybrid*. The various possible electronic structures are known as *canonical forms*. Homely analogy that has been suggested to facilitate the building up of a visual picture of resonance is a *mule*, which is a hybrid of a donkey and a horse. Just as the characteristics of a mule are fixed, so the properties of a resonance hybrid are fixed, with no oscillation between the contributing structures.

Some typical examples of substances which can be represented as resonance hybrids are given below :

(a) **Carbon dioxide.** Carbon dioxide molecule, for instance, can be represented by the three possible structures shown below :



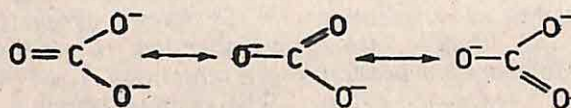
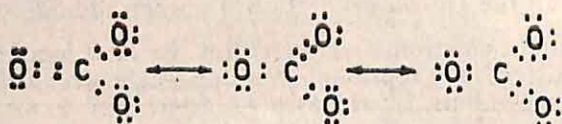
The actual structure of carbon dioxide is a resonance hybrid of the three structures.

The formula of carbon dioxide, for a long time, was thought to be $\text{O}=\text{C}=\text{O}$. If this was the correct formula, the bond distances in carbon dioxide ought to be equal to the sum of the double bond covalent radii [of carbon (0.67\AA), and oxygen (0.55\AA)]. This calculated bond length of 1.22\AA is not in agreement with the measured value of 1.15\AA . Moreover, the bond energy of the $\text{C}=\text{O}$ bond is 724 kJ mol^{-1} , so that the calculated heat of formation of carbon dioxide, if its structure is $\text{O}=\text{C}=\text{O}$, would be 1448 kJ mol^{-1} . The actual measured value is 1602 kJ mol^{-1} .

(b) Carbon monoxide.



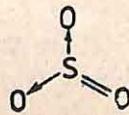
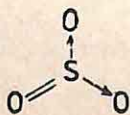
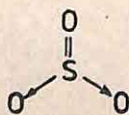
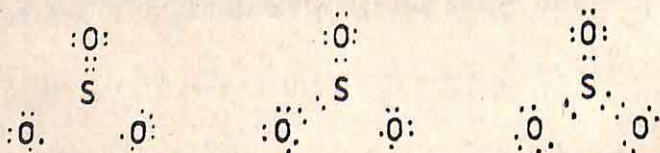
(c) Carbonate ion.



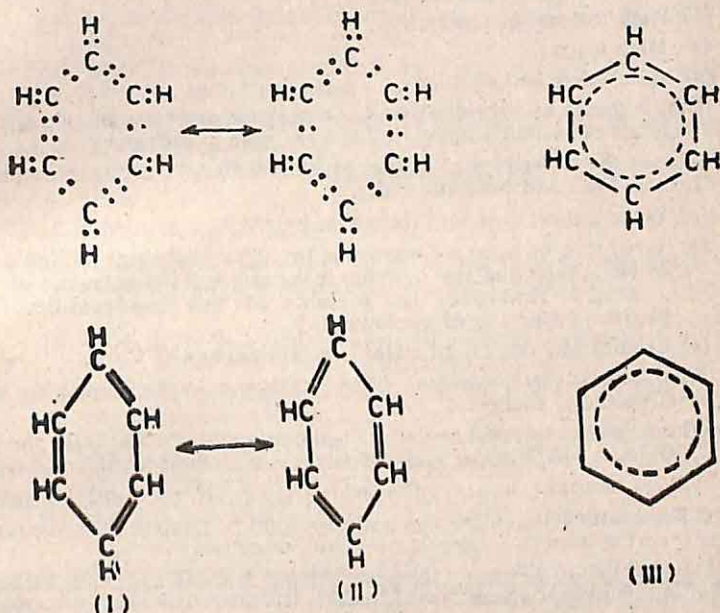
(d) Sulphur dioxide.



(e) Sulphur trioxide.



(f) Benzene.



QUESTIONS

(A) Essay Type :

1. What is a chemical bond ? Why do atoms combine to form compounds ?
2. (a) Name the various types of bonds which can be formed.
(b) Explain the formation of a chemical bond between two hydrogen atoms. What types of forces operate in the molecule. Do they lead to the stability of the molecule ?
(c) Why does helium not form diatomic molecules ?
3. Write a short essay on orbital concept of covalent bond formation.
4. What is meant by an ionic bond ? What are the conditions for the formation of this type of bond ?
5. (a) What is meant by sigma and pi bonds ?
(b) Define bond length and bond energy.
(c) What are the characteristics associated with compounds containing ionic bond ?
6. What is a covalent bond ? Explain its formation in terms of atomic orbital overlapping. What are the characteristics associated with compounds containing covalent bonds ?
7. (a) Write a note on co-ordinate bond.
(b) What is meant by electronegativity ? How does it help in interpreting the polarity of covalent bond ?
(c) What do you understand by dipole moment ? Give its significance.
8. What is a hydrogen bond ? What are the characteristics associated with compounds containing hydrogen bonds ?

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9. What is meant by metallic bond? How does "electron gas model" explain the following characteristics of metals?

- (a) High electrical conductivity,
- (b) High thermal conductivity,
- (c) High lustre,
- (d) Malleability and ductility.

10. That is meant by hybridisation? Discuss the geometry of sp^3 , sp^2 and sp hybrid orbitals of carbon atom giving one example in each case.

11. Discuss the underlying principles of VSEPR theory, citing examples of BeF_2 , BF_3 , CH_4 , H_2O and NH_3 molecules.

12. (a) Write a short note on "resonance hybrid."

(b) What type of bond is responsible for abnormally high boiling points of H_2O , NH_3 and HF ? What is the cause of the existence of such a bond? How does the presence of this bond influence the physical properties of compounds?

(c) Explain why density of water is maximum at $4^\circ C$?

13. What is meant by a covalent bond? Discuss its formation in terms of decrease of potential energy.

14. What is meant by bond angle? The bond angle in CH_4 , NH_3 and H_2O are 109.5° , 107° and 104.5° respectively. How do you account for this difference?

15. What is meant by sp , sp^2 , sp^3 hybridisation? Give suitable examples.

16. Differentiate between a sigma and pi bond? Explain why the former is stronger than the latter?

17. It is possible to give more than one valence bond structure for carbonate ion. What is this phenomenon termed? Give the canonical forms of carbonate ion.

18. (a) Why do ionic compounds have higher melting points than covalent compounds?

(b) Why is the dipole moment of NH_3 more than that of NF_3 ?

19. "The shape of a covalent molecule depends upon the number of electrons present in the outer shell of the central atom". How will you justify this statement?

20. Explain the following:

(a) The dipole moment of carbon dioxide molecule is zero but that of sulphur dioxide is $1.6D$.

(b) Density of ice (solid water) is less than that of liquid water.

(c) Sigma bond is stronger than a pi bond.

(d) Covalent bonds are directional; whereas ionic bonds are non-directional.

21. Give examples of:

(a) Two unlike atoms that form a non-polar covalent bond.

(b) Two unlike atoms that form a polar covalent molecule.

(c) Two molecules with tetrahedral geometry.

(d) A vertical sequence in which the electronegativity increases from top to bottom.

(e) Two molecules with linear geometry.

(f) Two molecules with triangular geometry.

(B) Objective Type :

22. Point out the correct statement in each of the following:

(a) When two dissimilar atoms combine to form a compound the covalent bond is polar.

- (b) A polar bond is formed between two atoms which have similar electronegativities.
- (c) By the lateral overlapping of p -orbitals, sigma bond is formed.
- (d) When two electron clouds overlap along their axis, a sigma bond is formed.
- (e) When two atoms approach to form a bond between them, the potential energy decreases.
- (f) Dipole-induced dipole type of interaction is stronger than ion-dipole interaction.
- (g) Ionic compounds conduct electricity quite well in the molten state.

23. Complete the following :

- (a) The tetravalency of carbon requires four equivalent atomic orbitals. These are produced by the..... of..... orbitals.
- (b) Bond formation between any two atoms is the result of..... of the orbitals of the two concerned atoms.
- (c) A double bond between two carbon atoms is made up of a..... bond..... and a..... bond.
- (d) In the carbon atom there are..... outer electrons. If bonding can be accounted for by sp^3 hybrid orbitals there will be..... bonds at angles of $109^\circ 5'$.
- (e) The four orbitals $2s, 2p_x, 2p_y, 2p_z$ can be mixed or as we say..... to give four equivalent orbitals.
- (f) Hydrogen bonds are formed between the hydrogen atom of the same or different molecule with..... electronegativity and..... size.
- (g) Electronegativity is a measure of the electron..... power of an element in a chemical bonding.
- (h) Intermolecular hydrogen bonding or association..... the boiling points of compounds.
- (i) The bonding together of atoms by the transfer of electrons is called bonding and the force of attraction between oppositely charged ions is known as..... forces.
- (j) In the formation of a molecule, generally the constituent atoms try to acquire.....
- (k) Acetylene is a linear ; molecule while methane is a..... molecule.
- (l) The lower density of ice than water is due to the formation of..... molecule due to.....
- (m) The element having the electronic configuration of $1s^2 ; 2s^2, 2p^6 ; 3s^1$ has the valency.....
- (n) An atom which loses electron is said to be..... ; while an atom which gains electrons is said to be.....
- (o) The type of hybridisation occurring in BeF_2 is.....
- (p) The bond formed between two atoms one of low ionisation potential and the other of high electron affinity is.....
- (q) Element..... has the highest electron affinity value.
- (r) BCl_3 undergoes..... hybridisation.

24. Match the two rows 'A' and 'B'

'Row A'

'Row B'

1. Sigma Bond.

1. Tetrahedral.

2. Covalent bond.

2. Trigonal.

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- | | |
|-------------------------------|-------------------------------|
| 3. Ionic bond. | 3. Linear. |
| 4. Ionic bond. | 4. Transfer of electrons. |
| 5. Geometry of sp^3 hybrid. | 5. Donating an electron pair. |
| 6. Geometry of sp^2 hybrid. | 6. Sharing of the electrons. |
| 7. Geometry of sp hybrid. | 7. Lateral overlapping. |
| 8. Co-ordinate bond. | 8. Axial overlapping. |

25. Given a list of type of bonds (A) on the left side and a list of compounds (B) on the right hand side, use the compounds only once and match the two 'A' and 'B'.

'Row A'

1. Ionic.
2. Single covalent.
3. Double covalent.
4. Triple covalent.
5. Co-ordinate covalent.
6. Hydrogen bond.
7. Resonance hybrid.

'Row B'

1. Water.
2. Ammonium ion.
3. Calcium chloride.
4. Methane.
5. Ethylene.
6. Carbon dioxide.
7. Nitrogen.

(C) Problems :

26. An atom of A forms an ionic bond with an atom B by complete transfer of one electron to B. Calculate the dipole moment of the bond, if the inter-nuclear distance is 200 Å. (The charge on the electron is 4.802×10^{-10} esu).

(Ans, 9.604 D)

27. The dipole moment of HBr is 0.78D and its bond distance is 1.41 Å. Calculate the percentage of ionic character of HBr bond.

(Ans. 11.46%)

States of Matter

5.1. INTRODUCTION

In general, matter may be defined as anything that has mass and occupies space. It is known to exist in three states—solid, liquid and gaseous. However, there is no sharp boundary between the various states, and in most cases a substance can be made to exist in any one of the three states by variation of temperature and pressure. For instance, water, a liquid at ordinary conditions of temperature and pressure, can be converted into solid state (ice) by cooling to 273K at atmospheric pressure or into gaseous state (steam) by heating to 373K at atmospheric pressure. Moreover, a substance under certain conditions may exist in all the three states simultaneously. For instance, at the freezing point of water (273K), solid ice, liquid water and water vapour all coexist.

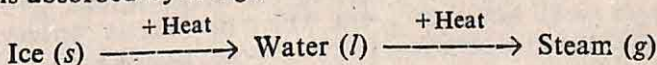
A substance, in general, is considered to be a :

(a) **Gas**, if its boiling point is below the room temperature under atmospheric pressure.

(b) **Liquid**, if its freezing point is below the room temperature under atmospheric pressure.

(c) **Solid**, if its melting point is above the room temperature under atmospheric pressure.

When a solid changes into a liquid or a liquid changes into a gas, heat is absorbed by it *e.g.*,



Thus, a given quantity of a substance possesses more energy in gaseous state than in liquid state and far more than in solid state.

5.2. CHARACTERISTICS OF THREE STATES OF MATTER

Gaseous State. (i) It is the *least ordered state* of matter since molecules in gaseous state do not occupy definite positions.

Hence, gas has no definite shape.

(ii) *The intermolecular voids are very large in a gaseous state* since the molecular forces of attraction in gases are very weak.

(iii) *The gaseous molecules can have all the three types of motion, viz., translational, rotational, and vibrational (see Fig. 5.1).* Consequently, the kinetic energy possessed by molecules in this state is very high.

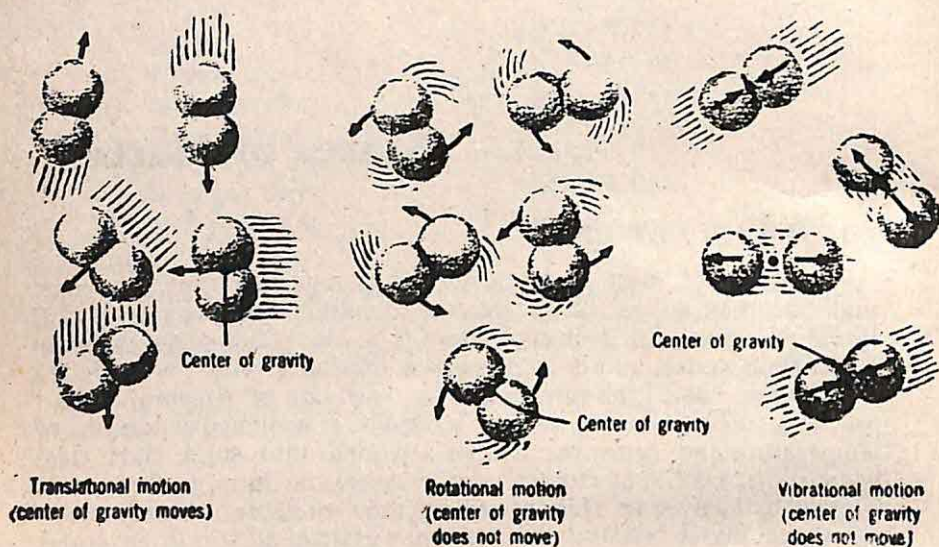


Fig. 5.1. Types of molecular motion. The diagram depicts diatomic molecules, and in the case of vibrational motion the atomic nuclei oscillate about an "imaginary" centre of gravity of two.

(iv) *Gases are easily and highly compressible* because the matter in the gaseous state is not compact.

(v) *Gases are indefinitely expansible* because the matter in the gaseous state is in kinetic motion. Evidently, a gas will occupy the entire volume of any vessel in which it is confined.

(vi) *Gases exert pressure (a force) on the interior walls of vessels in which they are confined.* In other words, gases exert a pressure on all boundaries with which they are in contact. Pressure is due to the hits recorded by the moving gaseous molecules on the walls of the vessel.

(vii) *Gases possess very low densities* because of weak intermolecular forces and large voids in between their molecules. Generally speaking, under ordinary conditions, gases are about one thousandth as dense as liquids.

(viii) *Gases diffuse*, or disperse, into each other so completely that all ordinary mixtures of gases are homogeneous.

(ix) *A gas has no boundary surface* on account of random motion of its molecules. Hence, a gas has neither a definite shape nor a definite volume.

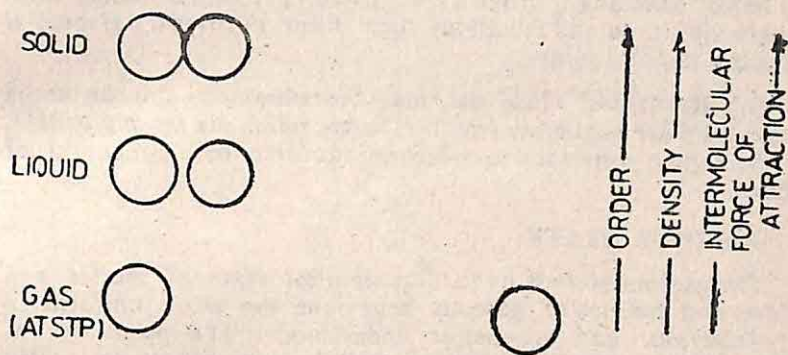


Fig. 5'2. Average distance between molecules in the three states of matter.

(x) Nearly all gases liquefy if they are cooled sufficiently. The removal of thermal energy from a gas decreases the kinetic energy of the molecules thereby allowing the intermolecular forces to increase their influence.

Liquid State. (i) Liquids consist of molecules in constant motion, although the molecular motion is more restricted than it is in ordinary gases. Liquid molecules can have rotatory motion in addition to vibratory motion. They have some translatory motion as well. Thus, *the liquid state is much more ordered than the gaseous state.*

(ii) The intermolecular forces are very significant in ordinary liquids, because the molecules are so close together.

(iii) The molecules constituting a liquid are not so rigidly fixed. Hence, *a liquid has no definite space.* It takes the shape of the vessel in which it is placed.

(vi) A molecule within a liquid is never an independent particle, because its physical behaviour is closely related to that of its neighbours to which it is strongly attracted. Thus, the molecular forces in liquid molecules are strong enough to prevent their separation from one another. Consequently, a liquid has *definite volume.*

(v) Nearly all pure liquids solidify if they are cooled sufficiently. The removal of thermal energy from a liquid decreases the kinetic energy of the molecule, thus allowing the intermolecular forces to increase their influence.

Solid State. (i) *The solid state is the most ordered state of matter.* The molecules of a solid are fixed rigidly in definite positions in a crystal lattice. Therefore, *a solid has a definite shape.*

(ii) The constituent particules of a solid are held close together by strong intermolecular force of attraction, and there is little or no void (or space) between them.

(iii) The constituents of a solid possess vibrational motion. They hardly have any translatory or rotatory motion. Thus, they can only vibrate to and fro about their fixed positions. Hence, a solid has a definite volume.

(vi) Because of close packing, the intermolecular distances in solid state are negligibly small. Hence, solids are incompressible, i.e., offers great resistance to a deforming force or application of pressure.

5.3. GASEOUS STATE

The gaseous state is by far the simplest state of matter and the laws and theories of gaseous behaviour are more uniform in their behaviour and are better understood. The properties of gases can be described in terms of certain generalisations, called "gas laws". Some important gas laws are :

1. **Boyle's law** (1662). It states that "*the volume of a given mass of a gas is inversely proportional to the pressure, if the temperature remains constant.*" Expressed mathematically,

$$P \propto \frac{1}{V}$$

or

$$PV = \text{constant (at constant temperature).}$$

Consequently, if volume, V_1 of a given mass of a gas at a pressure P_1 changes to V_2 when pressure is changed to P_2 , at constant temperature, then

$$P_1V_1 = P_2V_2 = \text{constant.}$$

2. **Charles's law** (1787). This law states that "*the volume of a given mass of a gas increases, or decreases by $1/273$ of its volume at 0°C for each degree centigrade rise, or fall in temperature, if the pressure remains constant.*" Expressed mathematically,

$$V_t = V_0 \left(1 + \frac{t}{273} \right)$$

or

$$V_t = \frac{V_0(t+273)}{273}$$

where V_t is the gas volume at $t^\circ\text{C}$ and V_0 the volume at 0°C .

This expression shows that if a gas could be obtained at -273°C , it would have a zero volume. In practice, however, all gases liquefy and/or solidify at temperatures much above -273°C . This temperature, at which, theoretically, a gas would have no volume is known as absolute zero. On this scale, called Absolute or Kelvin scale of temperature, K is equal to -273°C , or in general

$$K = ^\circ\text{C} + 273.$$

If the mathematical expression of Charles's law is written using Absolute scale temperature instead of $^{\circ}\text{C}$, then

$$V_1 = \frac{V_0 T}{273}$$

or
$$\frac{V_1}{T} = \frac{V_0}{273}$$

Thus, if V_1 is the volume of a given mass of a gas at absolute temperature T_1 and V_2 is the volume of the same gas at T_2 , then

$$\frac{V_1}{T_1} = \frac{V_0}{273}$$

and
$$\frac{V_2}{T_2} = \frac{V_0}{273}$$

$\therefore \frac{V_1}{T_1} = \frac{V_2}{T_2}$

or
$$\frac{V}{T} = \text{constant (if pressure is constant)}$$

This means that "*the volume of a given mass of a gas is proportional to the absolute temperature, if the pressure remains constant*" which is another statement of Charles's law.

3. The gas equation. Charles's and Boyle's law can be combined together into one general expression which is known as the gas equation. Suppose a given mass of gas has a volume of V_1 at a pressure P_1 , and it has a volume V at a pressure P_2 , if the temperature is kept constant. Then,

$$P_1 V_1 = V P_2 \quad (\text{by Boyle's law})$$

If now, the temperature at which V is measured is changed from $T_1\text{K}$ to $T_2\text{K}$ then the new volume of the gas, V_2 , will be given by the relationship,

$$\frac{V}{T_1} = \frac{V_2}{T_2} \quad (\text{by Charles's law})$$

Substitution of the value of V from one of these equations into the other gives the expression.

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or in general,
$$\frac{PV}{T} = \text{a constant } (k)$$

where (k) is a constant.

The value of k depends on the mass of the gas considered and on the units in which P and V are expressed. If 1 mole of gas is considered it is generally written as R and the gas equation then becomes,

$$PV = RT \quad (\text{For 1 mole of gas})$$

R is known as the *universal gas constant*.

Since 1 mole of gas at STP (0°C or 273K and 1 atmosphere pressure) occupies a volume of 22.4 litres. Therefore,

$$R = \frac{PV}{T} = \frac{1 \times 22.4}{273} \\ = 0.0821 \text{ litre atmosphere per degree per mole.}$$

The cgs units of R can be obtained as follows :

$$R = \frac{\text{Pressure} \times \text{Volume}}{\text{Temperature}} = \frac{(\text{Force/Area}) \times \text{Volume}}{\text{Temperature}} \\ = \frac{\text{Force} \times \text{Length}}{\text{Temperature}} = \frac{\text{Work}}{\text{Temperature}}$$

Thus, the units of R is work per degree. In cgs system this is generally expressed in ergs per degree (1 erg being the work done when a force of 1 dyne acts through a distance of 1 cm).

We know a pressure of 1 atmosphere = $76 \times 13.6 \times 981$ dyne cm^{-2} , and $V = 22.4$ litres = $22,400 \text{ cm}^3$. Therefore in cgs units,

$$R = \frac{76 \times 13.6 \times 981 \times 22,400}{273} \text{ ergs per degree per mole.} \\ = 8.32 \times 10^7 \text{ ergs per degree per mole.} \\ = 8.32 \text{ Joules per degree per mole.} \\ = 1.987 \text{ calorie per degree per mole.}$$

(\because 1 calorie is equal to 4.18×10^7 ergs)

If n moles of a gas is considered, the corresponding gas equation would be :

$$PV = nRT \quad (\text{For } n \text{ moles})$$

4. Dalton's law of partial pressures. Dalton found, in 1801, that "the total pressure exerted by a mixture of gases, which do not interact, is the sum of the pressures which each gas would exert if it were present alone in the entire volume occupied by the mixture." The pressure exerted by a gas if it were present alone in the entire volume occupied by the mixture is called *partial pressure*. Thus, if $P_1, P_2, P_3, \dots, P_n$ are the partial pressures of the different gases present in a mixture, then, the total pressure, P , of the gaseous mixture is given by

$$P = P_1 + P_2 + P_3 + \dots + P_n$$

The law of partial pressure is often used to find the pressure exerted by a dry gas from the knowledge of the pressure exerted by moist gas (a mixture of the dry gas and water vapour). In this case

Pressure of moist gas = Pressure of dry gas + Pressure of water vapour.

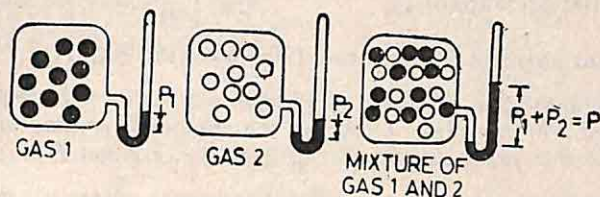


Fig. 5.3. Illustration of Dalton's law of partial pressures. Total pressure (P) exerted by a mixture of two gases is equal to sum of their partial pressures ($P_1 + P_2$) i.e., when present alone in the entire container.

The pressure of the water vapour, at any given temperature, is also known as *aqueous tension*.

\therefore Pressure of moist gas = Pressure of dry gas + Aqueous tension
or Pressure of dry gas = Pressure of moist gas - Aqueous tension.

Example 5.1. A mixture of gases at 760 mm Hg pressure contains 65.0% N_2 , 15.0% O_2 and 20.0% carbon dioxide by volume. What is the partial pressure of each gas in mm Hg?

Partial pressure of N_2 = $760 \text{ mm} \times 65/100 = 494 \text{ mm Hg}$.

Partial pressure of O_2 = $760 \text{ mm} \times 15/100 = 114 \text{ mm Hg}$.

Partial pressure of CO_2 = $760 \text{ mm} \times 20/100 = 152 \text{ mm Hg}$.

Example 5.2. In a gaseous mixture at 300K, the partial pressures of the components are as follows: $H_2 = 200 \text{ mm Hg}$; $CO_2 = 150 \text{ mm Hg}$; $CH_4 = 320 \text{ mm Hg}$; $C_2H_4 = 105 \text{ mm Hg}$. What is the total pressure of the mixture and the volume percent of hydrogen?

Total pressure of mixture = Sum of partial pressures.
= $200 + 150 + 320 + 105 = 775 \text{ mm}$.

Volume fraction of hydrogen = $\frac{\text{Partial pressure of } H_2}{\text{Total pressure of mixture}}$
= $\frac{200 \text{ mm}}{775 \text{ mm}} = 0.258 \text{ or } 25.8\%$.

Example 5.3. A 200 ml flask contained oxygen at 200 mm Hg pressure, and a 300 ml flask contained nitrogen at 100 mm Hg pressure. The two flasks were then connected so that each gas filled their combined volume. Assuming no change in temperature, what was the partial pressure of each gas in the final mixture and what is the total pressure?

Total volume = $200 + 300 = 500 \text{ ml}$.

Partial pressure of gas = $\frac{\text{Initial pressure} \times \text{Initial volume}}{\text{Final Volume}}$

$$\therefore \text{Partial pressure of O}_2 = \frac{200 \times 300}{500} = 120 \text{ mm Hg.}$$

$$\text{and partial pressure of N}_2 = \frac{100 \times 300}{500} = 60 \text{ mm Hg.}$$

$$\therefore \text{Total pressure of mixture} = 120 + 60 = 180 \text{ mm Hg}$$

Example 5.4. 100 ml of oxygen was collected over water at 296K and 800 mm Hg. Compute the standard volume of the dry gas. Vapour pressure of water at 296K is 21.2 mm Hg.

Pressure of dry gas = Total pressure - Vapour pressure of water.

$$= 800 - 21.1 = 778.9 \text{ mm (or 779 mm).}$$

In order to calculate volume of dry gas under standard conditions (273K and 760 mm Hg), we use gas equation

$$P_1 V_1 / T_1 = P_2 V_2 / T_2$$

(Given condition)

$$P_1 = 779 \text{ mm}$$

$$V_1 = 100 \text{ ml}$$

$$T_1 = 296 \text{ K}$$

(Standard conditions)

$$P_2 = 760 \text{ mm}$$

$$V_2 = ?$$

$$T_2 = 273 \text{ K}$$

$$\text{or} \quad \frac{779 \times 100}{296} = \frac{760 \times V_2}{273}$$

$$\text{or volume at STP, } V_2 = \frac{779 \times 100 \times 273}{296 \times 760} \text{ ml.}$$

$$= 95.5 \text{ ml.}$$

5. Graham's law of gaseous diffusion. The most striking characteristics of gases is their ability to diffuse. Diffusion means, literally, spreading out. A gas can escape through a small aperture or hole and this is often referred to as effusion (effuse means to leak). Graham, in 1846, compared the rates at which various gases diffused through porous pots, and from his findings he gave law of diffusion which states that "the rate of diffusion (or effusion) of a gas, at constant temperature and pressure, is inversely proportional to the square root of its density". In mathematical form,

$$\text{Rate of diffusion} \propto \sqrt{\frac{1}{\text{Density}}}$$

By comparing the rates of diffusion of two gases A and B, it is possible to measure the density of one if that of the other is known for

$$\frac{\text{Rate of diffusion of A}}{\text{Rate of diffusion of B}} = \sqrt{\frac{\text{Density of B}}{\text{Density of A}}}$$

Example 5.5. *Hydrogen diffuses 4.7 times as fast as carbon dioxide, calculate the density of carbon dioxide if that hydrogen is 1.*

$$\frac{\text{Rate of diffusion of H}_2}{\text{Rate of diffusion of CO}_2} = \sqrt{\frac{\text{Density of CO}_2}{\text{Density of H}_2}}$$

$$\text{or} \quad 4.7 = \sqrt{\frac{\text{Density of CO}_2}{1}}$$

$$\text{or} \quad \text{density of CO}_2 = (4.7)^2 = 22 \text{ (Approx.)}$$

5.4. THE KINETIC-MOLECULAR THEORY OF GASES

In order to account for the properties of gases (such as compressibility, expansionability, and diffusability) a concept known as kinetic-molecular theory was developed between 1860 and 1890 mainly by Clausius, Clerk Maxwell and Boltzmann. The main postulates of this theory and some of their interpretations are given below.

(i) *A gas consists of a vast number of very small particles (molecules) which are in rapid and continuous motion in all directions, continually undergoing collision with each other and with the walls of the vessel but moving in straight lines between*

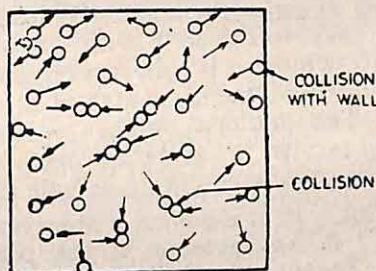


Fig. 5.4. Kinetic model of a gas.

collisions. Thus, in any sample of a gas at any instant molecules are moving at all possible speeds and in all possible directions, (i.e., motion is completely chaotic).

(2) *The pressure exerted by a gas on the walls of its containing vessels is due to bombardment by the moving particles.*

(3) *The collisions between particles are perfectly elastic, i.e., the speed of a molecule is the same after a collision as before and only the direction of motion being changed. This assumption is necessary, or else it could be argued that the rebounding molecules would gradually slow down, and the gas would liquefy. However, under constant pressure and temperature a sample of gas does not liquefy upon standing over any period of time.*

(4) *Attractive forces between molecules are negligible as the pressure upon a gas is released, (i.e., lowered), the gas expands.*

If the force of attraction between the molecules were appreciable, the gas would have resisted expansion.

(5) The molecules are so small as compared with the average distance travelled between consecutive collisions (which is known as the *mean free path*) that *the space actually occupied by the molecules is negligible as compared to the volume of the gas as a whole*. In simple treatments the molecules are regarded as points. The relatively large volume of gas which is obtained on evaporating a liquid suggests that this assumption is justified.

(6) *The average kinetic (motion) energy of the molecule is proportional to the absolute temperature*. A gas in a closed container (constant volume) at constant temperature exerts a constant pressure. If one increases the temperature of a confined gas by adding heat energy, the pressure is observed to rise (Gay-Lussac's law). The increase in pressure reflects an increase in molecular velocity, which in turn indicates that the heat energy has resulted in the increased kinetic energy of the molecules.

The gas laws may be readily explained in the light of the kinetic-molecular theory.

(1) *Boyle's law*. The pressure exerted by a gas upon the walls of its container is caused by the bombardment of the walls by rapidly moving molecules and varies directly with the number of molecules confined in a given volume. Reducing the volume of a given mass of a gas, say, to one-half with double the number of molecules per unit volume. It follows that the number of impact (or hits) per unit time upon the same area of the walls surface will also be doubled. The doubled number of impacts per unit area will, consequently, result in twice as much pressure. This is in accordance with Boyle's law relating volume and pressure.

(2) *Charles's law*. It is a common observation that a rise in temperature results in an increase in the pressure of a gas at constant volume, because the average kinetic energy of the molecules is raised with the increase in temperature. An increase in average velocity of molecules results in more frequent and harder impacts upon the walls of the container, i.e., greater pressure. However, if the pressure remains constant with increasing temperature, the volumes must increase so that each molecule on the average travels farther before hitting the wall. The smaller number of molecules striking the walls at a given time is counterbalanced by the greater force with which each molecule hits, thereby making it possible for the pressure to remain constant. Moreover, since the absolute temperature of a gas is a measure of the average kinetic energy of molecules, so, increase in volume by increasing temperature will be proportional to absolute temperature.

(3) *Dalton's law*. In a mixture of gases the molecules of one component will bombard the walls of the container just as frequently in the presence of other kinds of molecules as in their absence.

Thus, the total pressure of a mixture of gases will be sum of the partial pressures of the individual gases.

(4) *Graham's law of diffusion.* The fact that the molecules of a gas are in rapid motion and that the free space between the molecules is very great explains the phenomenon of diffusion. At the same temperature, molecules of different gases have the same average kinetic energy ($\frac{1}{2}mv^2$). This means that molecules of small mass move with higher velocities than those of large mass. Thus, if v_1 and v_2 are the average velocities of molecules of two gases of mass m_1 and m_2 respectively. Then, at constant pressure

$$\frac{1}{2} m_1 v_1^2 = \frac{1}{2} m_2 v_2^2$$

$$\text{or} \quad mv^2 = \text{constant.}$$

$$\text{or} \quad v \propto \sqrt{\frac{1}{m}}$$

Thus, velocity of a molecule is inversely proportional to its mass. Consequently diffusion rate of gases are related inversely to square root of their molecular masses* and hence densities.

5.5. KINETIC GAS EQUATION

From the assumption of kinetic-molecular theory of gases, it is possible to derive a mathematical expression known as *kinetic gas equation*.

$$PV = \frac{1}{2} mNv$$

Here m is the mass of one molecule of gas, N is the number of molecules in volume V ; P is the pressure exerted by the gas and V is the velocity of gas molecules, known as *root mean square velocity*.

The above expression can be written as :

$$\begin{aligned} PV &= \frac{2}{3} \times \frac{1}{2} mNv^2 = \frac{2}{3} \times N \times \frac{1}{2} mv^2 \\ &= \frac{2}{3} \times \text{Kinetic energy of } N \text{ molecules of gas.} \\ &= \frac{2}{3} \times \text{Kinetic energy of 1 mole of gas.} \end{aligned}$$

But for 1 mole of any gas

$$PV = RT$$

*It may be pointed here that [the hydrogen is the lightest and, therefore, diffuses most rapidly of all the gases. The average velocity of its molecules at room temperature is about 1.8 kilometre per second. However, the diffusion rates are much lower than this due to collision between molecules, of which there are about 11 billion per molecule per second in hydrogen gas at standard conditions. Hydrogen molecules travel about 17×10^{-6} cm between collisions, and on average are halted about 60,000 times in travelling one centimeter.

$\therefore \frac{3}{2}$ K.E. of 1 mol of gas $= RT$

or K.E. of 1 mole of gas $= 3RT/2$

or Kinetic Energy $\propto T$ (since R is a constant)

Thus, the kinetic energy of a gas is directly proportional to the absolute temperature and is independent of the nature or pressure of the gas. This is known as Maxwell's generalisation.

Since kinetic energy is proportional to square of velocity, so, it follows that :

$$v^2 \propto T$$

or

$$v \propto \sqrt{T}$$

i.e., molecular velocity of any gas is directly proportional to the square root of the absolute temperature. The motion of gas molecules is, therefore, called *thermal motion*.

At absolute zero, (i.e., $T=0K$), the kinetic energy will be zero. Hence, we can say that the *thermal motion of molecules ceases completely at absolute zero*.

5.6. MAXWELL'S DISTRIBUTION OF VELOCITIES

The individual molecules of a gas do not have the same velocity. This is because the molecules are very frequently colliding with one another and their velocities keep on varying. Most molecules have a velocity, close to the average, but some molecules may acquire considerably higher or lower velocities as a result of a series of favourable or unfavourable collisions. The distributions of velocities amongst the molecules of a gas was worked out, by Maxwell and Boltzmann, from the laws of

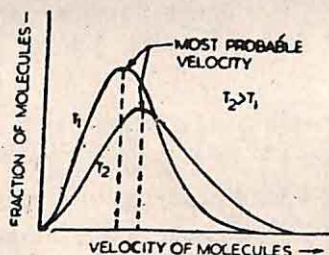


Fig. 5.5. The distribution of molecular velocities in a gas.

probability. Their findings are shown graphically in Fig. 5.5, in which fraction of molecules having various velocities are plotted against their velocities. From the curve it is clear that :

(a) The fraction of molecules with too low or too high velocities is very small.

(b) Maximum fraction of molecules possess velocities.

corresponding to the peak of the curve. This is known as the *most probable velocity*.

(c) At higher temperatures the fraction of molecules with higher velocities (and hence higher kinetic energies) increases whilst the fraction with average velocity, (i.e., most probable velocity) decreases.

5.7. DEVIATION FROM GAS LAWS

A perfect or ideal gas may be defined as one which strictly obeys the gas laws or the gas equation $PV = nRT$; but none of the

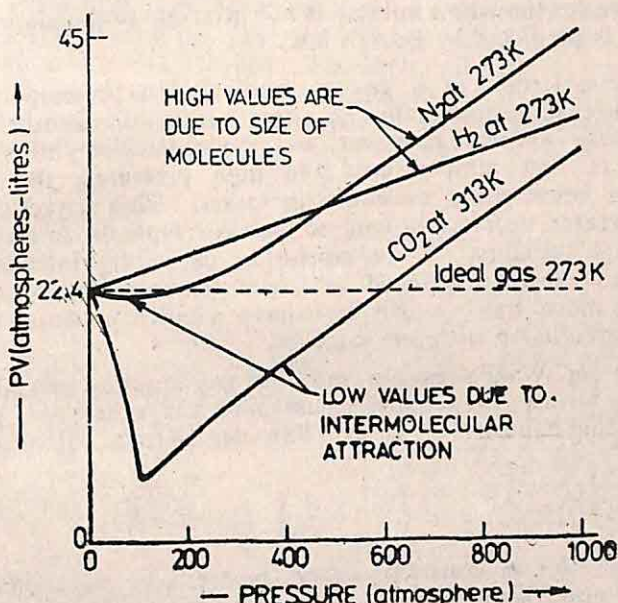


Fig. 5.6. The plot of product of PV versus P for 1 mole of gas at the temperature specified.

real gases is found to be perfect and all the gas laws are only approximately true. Thus, if Boyle's law is obeyed fully, the value of PV for a given quantity of gas should be constant at all pressures and the graph should be a horizontal line. However, actual values obtained for common gases like H_2 , N_2 , CO_2 , etc., is quite different and this is shown in Fig. 5.6.

The cause of these deviations from ideal behaviour may be attributed to the following *faulty assumptions* made in the kinetic molecular theory.

- (i) The actual volume occupied by the gas molecules is negligible as compared with the total volume of the container.
- (ii) The molecules exert no intermolecular attraction among themselves.

Both these assumptions are not true, particularly at low temperatures and high pressures. When gases under ordinary conditions of temperature and pressure are compressed, the volume is reduced by crowding of molecules closer together. This reduction in volume is really a reduction in the amount of empty space between the molecules. At high pressures, the molecules are crowded so closely together that the volume they themselves occupy is a large fraction of the entire volume of the gas. Because the volume of the molecules themselves is not compressed, only a small fraction of the entire volume (*i.e.*, total volume - volume of molecules themselves) can be affected by an increase in pressure. Thus, at high pressures the whole volume is not inversely proportional to the pressure as predicted by Boyle's law.

The molecules in a gas at relatively low pressure and high temperatures have practically no attraction for one another because they are far apart. However, as the molecules are crowded together at low temperatures and high pressures, the force of attraction between the molecules increases. This attraction causes slightly greater decrease in volume than corresponds to the increase in external pressure. The compression caused by inter-molecular attraction is more pronounced at lower temperatures because the molecules move more slowly and have smaller tendency to move apart after collision with one another.

Van der Waal's gave a modified gas equation by making two correction terms, one for the volume and the other for pressure. The modified equation is called Van der Waal's equation and is written as :

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT$$

where a and b are constant, called respectively as *coefficient of attraction* and *effective volume or co-volume* of the gas molecules.

59 LIQUID STATE

The molecules of a substance in the gaseous state are in constant and very rapid motion and the space between the molecules is large compared to the size of the molecules themselves. However, as the molecules of a gas are brought closer by increased external pressure, the average distance between the molecules is decreased and intermolecular attractive force become stronger. Also as a gas is cooled, the average velocity of the molecules decreases and their tendency to move apart after collision decreases. Consequently, if pressure is sufficiently high and the temperature is low enough, the intermolecular attraction overcomes the tendency of the molecules to move apart, and the gas molecules condense to the liquid state. Although the molecules in the liquid state attach or cling to one another, they still possess a limited amount of motion as reflected in the capacity of liquid, to flow and to take the shape of a container. The molecules in a liquid are held in such close contact by their mutual attractive

molecular forces that the volume of any liquid decreases very little with increased pressure and consequently liquids are relatively incompressible as compared to gases.

5.10. CHARACTERISTICS OF LIQUIDS

Some of the general properties of liquids are :

1. **Diffusion.** The molecules in a liquid are able to move past one another in random fashion, (*i.e.*, diffusion), but because of the much more limited freedom of molecular motion existing in liquids, they diffuse much more slowly than do gases.

2. **Evaporation.** It is a common observation that water placed in an open vessel decreases in volume upon standing. We say that evaporation has occurred. Similarly, all liquids evaporate when placed in open vessel. Evaporation of a liquid may be explained in terms of motion of molecules. At any given temperature, above the absolute zero, the molecules of a liquid move—

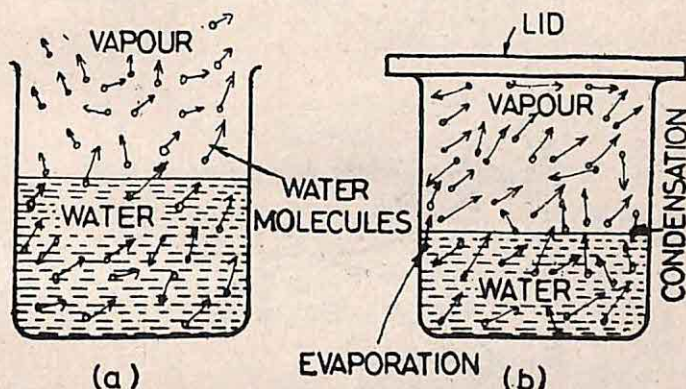


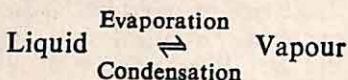
Fig. 5.7. (a) Molecules of water escape from the open beaker, evaporation occurs and the water level is lowered. (b) Molecules of water do not escape from the closed beaker and a dynamic equilibrium is reached.

some slowly, some at intermediate rates, and some very fast. A rapidly moving molecule near the surface of a liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape, (*i.e.*, evaporate) in the space above the liquid (*see* Fig. 5.7). Similarly, other fast moving molecules leave the liquid surface and appear in the gaseous state above the liquid as the process of evaporation continues.

During the process of evaporation molecules having highest kinetic energies keep on leaving the liquid phase, so, the average kinetic energy of the remaining molecules continue to fall. Hence, evaporation causes cooling. However, it may be pointed out that as the liquid evaporates, the fall in temperature of liquid is neutralised by the absorption of heat by the liquid from its surroundings and consequently, the temperature of the liquid

remains the same as the room temperature.

When the space above the liquid is limited (see Fig. 5.7 (b)), the molecules cannot escape into the open but strike the walls of the container, rebound, and may strike surface of the liquid where they may be trapped. The return of the molecules from the vapour state to the liquid state is known as *condensation*. As the evaporation proceeds, the number of molecules in the vapour state increase, and in turn the rate of condensation increases (see Fig. 5.8). The rate of condensation soon becomes equal to the rate of evaporation and the vapour in the closed container acquires an equilibrium with its liquid. This is called a *dynamic equilibrium*



because the two opposing processes of evaporation and condensation are in full operation and do not stop at any moment.

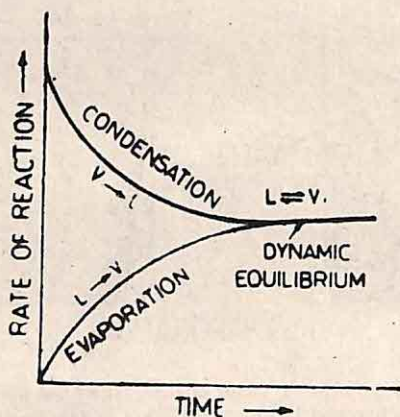


Fig. 5.8. Rates of evaporation and condensation of liquid molecules in a closed vessel, with elapse of time.

At the equilibrium the space above the liquid is said to be saturated with respect to molecules of the vapour. The pressure exerted by the vapour in equilibrium with its liquid at a given temperature is called the *vapour pressure of the liquid*. The magnitude of vapour pressure depends on the nature of the liquid and the temperature. Non-polar liquids (like chloroform, carbon tetrachloride, acetone, benzene, etc.) have high vapour pressures because of weak forces of attraction between their molecules. However, polar liquids (like water, alcohol, acetic acid, etc.) have comparatively lower vapour pressures due to relatively stronger dipole-dipole interaction between their molecules.

As the temperature of liquid is increased the average kinetic energy of the liquid molecules increases. Also the proportion of

molecules possessing extremely high energies, which are able to overcome the intermolecular forces of attraction, also increases. This is shown by shaded area in Fig. 5.9. Consequently, more molecules are now capable to escape into the space above the liquid surface and form vapour. This in turn, results in higher equilibrium vapour pressure of the liquid with increase in temperature. The variation of vapour pressure with temperature is shown in Fig. 5.11.

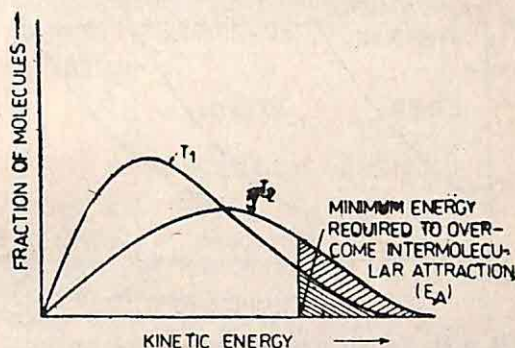


Fig. 5.9. Distribution of energies in liquids.

As the temperature of a liquid is raised, its vapour pressure increases till it becomes equal to the atmospheric pressure. At this point bubbles of vapour form within a liquid and rise to the surface where they burst, and the liquid is said to boil (see Fig.

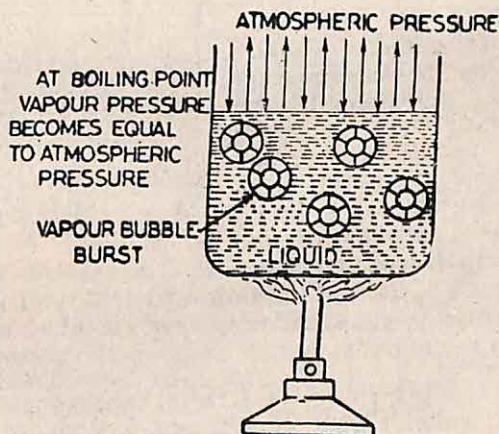


Fig. 5.10. At boiling point bubbles of vapour are formed within a liquid and rise to the surface where they burst.

5.10). Thus, *boiling point may be defined as the temperature at which equilibrium vapour pressure of a liquid becomes equal to the*

atmospheric pressure. If atmospheric pressure is varied, the boiling point of a liquid also varies. The normal boiling point of a liquid is that temperature at which its equilibrium vapour pressure becomes exactly equal to the standard atmospheric pressure of 760 mm Hg. A liquid may boil at temperatures higher than normal under external pressures greater than one atmosphere.

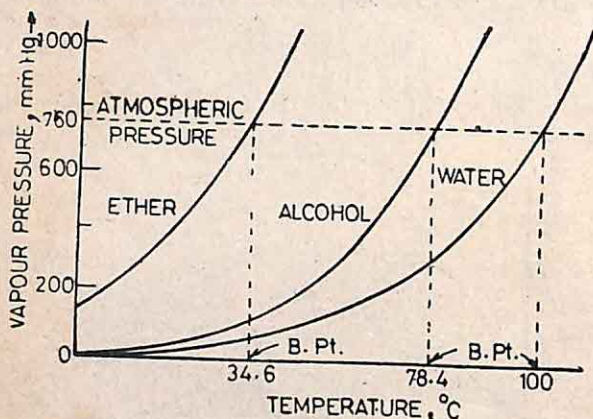


Fig. 5.11. Variation of vapour pressure of some common substance with temperature.

Conversely, the boiling point of a liquid may be lowered below normal by decreasing the pressure on the surface of the liquid below one atmosphere. The normal boiling points of ether, alcohol and water are 44.6, 78.4 and 100°C respectively as shown in Fig. 5.11.

3. Surface tension. The molecules within the bulk of a liquid (say A in Fig. 5.12) are attracted equally in all directions by the neighbouring molecules; and consequently the resultant intermolecular force of attraction on any one molecule within the liquid is zero. However, the molecules on the surface of a liquid (like B) are attracted only inwards and sideways. This unbalanced molecular attraction pulls some of the surface molecules into the bulk of the liquid and a condition of equilibrium is reached when the surface area is reduced to minimum.

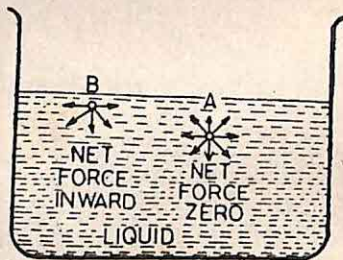


Fig. 5.12.

The surface of the liquid, therefore, behaves as if it were under a strain or tension. This contracting force is called **surface tension**. It is defined as the force in dynes acting on the surface of a liquid at right angles per centimeter length of surface. A small drop of liquid tends to assume a spherical shape due to surface tension since in a sphere the ratio of surface area to volume is minimum. Thus, we may define **surface tension** as the force which

causes the surface of a liquid to contract. Surface tension of a liquid depends upon the nature of molecules and the temperature.

4. **Viscosity** is a property of a liquid by virtue of which it offers resistance to its own flow. A liquid in a state of flow on a surface may be supposed to consist of a series of layers one above the other. A thin layer, immediately in contact with solid surface is almost stationary. Each succeeding layer moves with gradually increasing velocity. Thus, any two layers will move with different velocities. A faster layer is dragged back by its next slower layer with a certain force. Now consider two layers of a liquid separated by a distance d and moving with a velocity difference v , then force per unit area required to maintain this difference of velocity is given by

$$F = \eta \frac{v}{d}$$

where η = a constant, called coefficient of viscosity.

If $v = 1$ cm/sec; $d = 1$ cm; then $F = \eta$. Hence, coefficient of viscosity may be defined as *the force per unit area required to maintain a unit velocity difference between two parallel layers in the fluid which are one cm apart.* Thus, greater the co-efficient of viscosity, the more slow will be the flow of liquid and vice versa. The unit of viscosity is *Poise*.

5.10. INTERMOLECULAR FORCES

Molecules whose centres of positive and negative charges do not coincide, possess permanent electric dipole moment. The HCl molecule, because chlorine has a greater electronegativity than hydrogen, has a partial positive charge on the hydrogen. Hence, HCl molecule has a permanent dipole moment. The electrostatic attraction of the positive end of one HCl molecule for the negative end of the another constitute an attractive force.

An additional force of attraction between molecules, which occurs for non-polar molecules as well as polar molecules, is known as the van der Waal's attraction. Van der Waal's forces of attraction are due to the electrostatic attraction of the positive nucleus of one molecule for the electron cloud of a neighbouring molecule. In a non-polar substance, such as iodine and the inert gases, there is no initial dipoles; the molecules are electrically symmetrical. However, any slight relative displacement of the nuclei or the electrons in a molecule will give rise to an electrical dipole, and it is thought that, momentarily, such displacements are constantly occurring within molecules or atoms. In a hydrogen atom, for example, consisting of one proton and one electron, the charge distribution of the electron may not be absolutely symmetrical at any one particular instant. The electrical displacement, which establishes a dipole in a molecule is temporary and random. However, molecule having a dipole at any one instant, induces another dipole in a neighbouring molecule and an attractive force will be established between the two.

To illustrate the above explanation of origin of van der Waal's forces, let us consider that the electron distribution in molecule A for an instant is unsymmetrical and is concentrated towards one side of it (see Fig. 5.13). At this moment a temporary dipole exists in the molecule A. The molecule B in its vicinity, in turn, is distorted at the same moment with its nucleus attracted towards the negative end of molecule A and its negative end opposite from the negative end of molecule A. A mutual attraction between the nucleus of one molecule and the electron cloud of the other and a repulsion between the two nuclei and also a repulsion between the two centres of negative charge of the electron clouds take place. The constant motion of the electrons causes a shift so that in next instant, the concentration of negative charge in one molecule may shift to the other side. This has a corresponding effect on the distribution of charge within the other neighbouring molecule, resulting in creation of two new dipoles oppositely oriented within the two molecules. These nearly instantaneous fluctuating dipoles result in an attraction (called van der Waal's) attraction between the molecules.

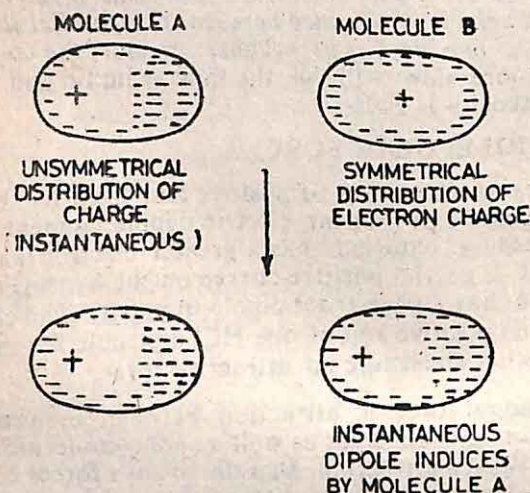


Fig. 5.13. Diagram showing van der Waal's attraction due to nearly instantaneous fluctuating dipoles.

The van der Waal's attraction is weak in nature and is significant only when molecules are very close together, i.e., very nearly in contact with each other. The van der Waal's attraction is opposed by (i) the repulsive force of the electron clouds of the adjacent molecules and (ii) the repulsion of the nuclei of neighbouring atom for one another. However, the attractive forces are somewhat stronger than the repulsive forces.

Trends. (1) *The magnitude of the van der Waal's attraction increases with increase in the number of electrons per molecule and, therefore, with the molecular mass.* This increase in intermolecular

attraction with molecular mass is reflected in the rise in boiling point in series or related substances such as He, Ne, Ar Kr, Xe, Rn, and as H_2 , F_2 , Cl_2 , Br, I_2 (see Table 5.1).

Table 5.1. Molecular masses and boiling points.

Substance	He	Ne	Ar	Kr	Xe	Rn
Mol. Mass	4.0	20.18	39.94	83.7	131.1	222
B. Pt. (K)	4.1	27.1	87.3	120.1	165.9	211.2

Substance	H_2	F_2	Cl_2	Br	I_2
Mol. Mass	2.016	38.0	70.91	159.8	253.8
B. Pt. (K)	20.3	86.0	238.4	331.8	457.4

(2) *The van der Waal's force acting between molecules is of decreasing effectiveness with an increase in temperature* since the additional thermal energy thus provided increases the motion of the molecules thereby overcoming the van der Waal's attractive force. Thus, it is the van der Waal's attraction that causes non-polar substances such as the noble gases and the halogens, to condense to liquids and to freeze into solids when the temperature is lowered sufficiently.

(3) *In general, liquid compound of discrete molecules, which have no permanent dipole moments, have low boiling points relative to their molecular masses* because only the weak van der waal's attraction must be overcome during vaporisation. Examples are the molecules of noble gases and halogens, and other symmetrical molecules such as CH_4 , SiH_4 , CF_4 , SiF_4 , SiF_6 and UF_6 . Molecular substances such as H_2O , HF, NH_3 , and C_2H_5OH (ethyl alcohol), which have permanent dipole moments, have high boiling points relative to their molecular masses.

5.11. SOLID STATE

When thermal energy is removed (i.e., cooled) from a molecular liquid, the molecules move less and less rapidly because their kinetic energy is being decreased. As more and more energy is removed from most liquids, the influence of the intermolecular attractive forces becomes stronger and stronger. The molecules, consequently, arrange themselves in the orderly geometric pattern of a solid. Whenever a true solid is formed by cooling a liquid the process is called freezing, or crystallization and the liquid is said to be frozen.

The freezing temperature of most liquids is well above absolute zero (0K) and since the molecules in the molecular solid have kinetic energy, we should infer that molecules in solid state possess a limited but definite degree of motion. Since the molecules in a solid are in the relatively fixed positions in space, the motion of each molecule is only a vibration (oscillation) about a fixed position. The orderly geometric arrangement of these vibrating molecules form a crystal lattice having a definite spatial structure.

Some liquids, however, do not solidify to produce rigid, geometric patterns (i.e., crystals). When these liquids are cooled to lower and lower temperatures, they gradually become more and more brittle, but they do not assume a distinct shape or structure. Such solids are called *amorphous* (because they do not have definite morphology).

Thus, solids may be described either as crystalline or amorphous. *Crystalline solids have a regular arrangement of particles in typical geometrical forms; whereas amorphous solids have a completely random particle arrangement.*

5.12. CHARACTERISTICS OF SOLIDS

Solids are characterised by definite shape, definite volume, noncompressibility, very slow diffusion rate, high rigidity and mechanical strength. The atoms, molecules or ions in solids are closely packed and they are held together by strong forces and hence cannot move about in random. A crystalline solid has a sharp melting point; while amorphous solids do not have. For example, on heating glass, an amorphous substance, it softens and then starts flowing without undergoing any abrupt or sharp change from solid to liquid state. Amorphous substances, in many respects, resemble liquids which flow very slowly at room temperatures. Strictly speaking, amorphous substances are regarded as *supercooled liquids* in which the force of attraction holding the molecules together is so great that the material is rigid but there is no regularity of structure.

Melting of solids. When a crystalline substance is heated sufficiently, the vibrational energy of some of the molecules becomes great enough to overcome the intermolecular forces holding the molecules in their fixed position in the crystal lattice, and the solid begins to melt (fuse). If heating is continued, all of the solid changes to the liquid state even though the temperature does not rise. The temperature at which the solid passes into liquid state and vice versa is known as the *melting* or *freezing point* of the solid.

The melting point of a solid reflects the strength of the forces of attraction between the building units present in the crystal. Thus, crystals composed of small symmetrical molecules (such as H_2 , O_2 , F_2) have low melting points because the intermolecular forces are of the weak van der Waal's type. On the other hand, crystalline solids build up of unsymmetrical molecules with permanent dipole moments (such as ice, sugar) melts at higher temperatures. Diamond is an atomic crystal in which the small carbon atoms are held together in the crystal lattice by strong covalent bonds and, consequently, the melting point of diamond is very high. The atoms in the crystals of metals are strongly bonded together by metallic bonds, which are nothing but modified form of covalent bonds. Hence, metals, in general, have high melting points. The ionic crystals also have high melting points because the electrostatic

forces of attraction between the ions in ionic solids are quite strong.

5.12. CLASSIFICATION OF CRYSTALS

Crystals on the basis of nature of forces which holds the crystal lattice together, can be classified into following four categories.

(i) **Ionic crystals.** The ionic crystal lattice consists of an array of positive and negative ions arranged in a characteristic pattern. The binding forces are the strong electrostatic bonds of positive and negative charges. Consequently, ionic crystals are hard and brittle. The amount of energy necessary to evaporate some typical ionic crystals to their separated ions is of the order of

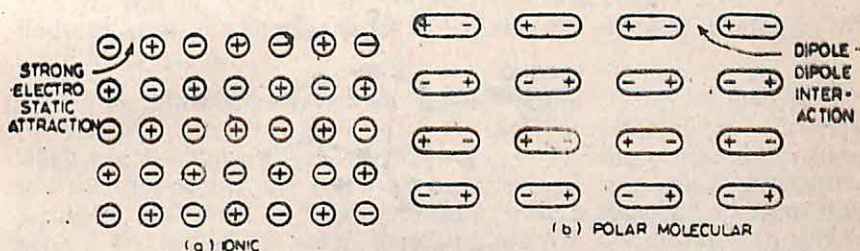


Fig. 5.14. Four types of crystalline structures.

800 kJ mol^{-1} . This very large binding energy is responsible for the fact that ionic crystals have vanishingly small vapour pressure at room temperature and melt and boil only at relatively high temperature. Ionic crystals are insulators in the solid state because all the ions occupy well-defined positions and are held by strong ionic

bonding and, therefore, a large energy is needed to dislodge them. However, in liquid state (molten form) ionic solids are good conductors because the arrangement of ions in liquid state is quite disorderly and this helps their movement under the influence of applied electric field.

Generally speaking, compounds formed by combining metals of group IA and group IIA and non-metals of group VIA and group VIIA form ionic crystals.

(ii) **Covalent crystals.** The covalent crystal lattice consists of an array of atoms that share electrons with their neighbouring atoms, i.e., atoms are linked together by a continuous system of strong covalent bonds which extend in fixed directions. The resulting crystals are a giant, compact, interlocking, three-dimensional structures called *macromolecule*. They are very hard and

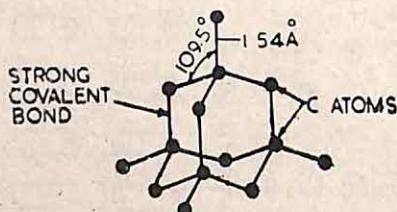


Fig. 5.15. Portion of a diamond crystal.

brittle, have rather high melting points and are non-conductors, e.g., diamond, silicon carbide, silicon dioxide, oxides of transitional metals. The structure of diamond is represented in Fig. 5.15.

In some crystals of this type the continuous network of covalent bond is two-dimensional and not three dimensional. For example, graphite whose structure is represented in Fig. 5.16. The

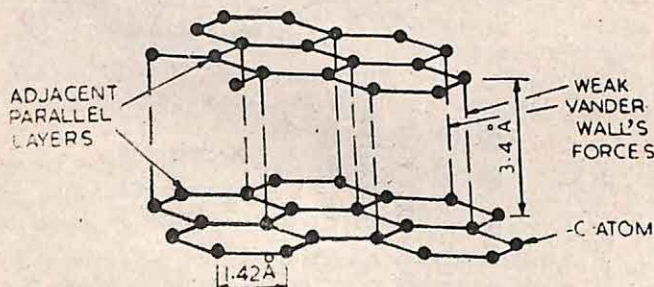


Fig. 5.16. Portion of a graphite crystal.

atoms are arranged in parallel planes 3.41 \AA apart. The atoms in the same plane arranged in the form of a network of regular hexagon. The C—C distance is about 1.42 \AA . Since, the distance between the adjacent layers is comparatively larger than the maximum permitted for a chemical bond, therefore, it is evident

that the layers are not held by chemical bond but by weak van der Waal's forces. As the forces between the different sheets of layers are feeble, so, rupture between the various layers can occur easily. This explains the soft and flaky nature of graphite. It may also be noted that each carbon atom is connected only to three other carbon atoms. In other words, the fourth valency of carbon atoms is unsatisfied. This makes graphite a good conductor of electricity.

(iii) **Metallic crystals.** The metallic crystal lattice consists of positive ion permeated by a cloud of valency electrons commonly referred to as the electron gas. The binding force is the attraction between the positive ions of the metal and the electron cloud. The valency electrons may be considered to have been donated by the atoms of the metal and belong to the crystal as a whole. These electrons are free to migrate throughout the crystal lattice giving rise to the high electrical conductivity associated with metals. Sodium, iron, tungsten, copper and silver are typical examples of metallic crystals.

(iv) **Molecular crystals.** The molecular crystal lattice consists of symmetrical aggregates of discrete molecules bound by relatively weak van der Waal's force between them. The molecular solids have low melting points, are relatively soft, volatile and good insulators. I_2 , solid CO_2 , solid H_2O (ice) and solid hydrogen belong to this type. The molecular solids may be polar or non-polar. In polar molecular crystals, there is the additional attraction between the oppositely charged parts of neighbouring molecules. The covalent chemical bond which binds the atoms within the molecules are much stronger than the forces which form the crystal lattice.

QUESTIONS

(A) Essay Type :

1. Distinguish between the three states of matter.
2. State and explain Boyle's law, Dalton's law of partial pressures, and Graham's law of diffusion.
3. Summarise the kinetic-molecular theory as it applies to gases. Explain various gas laws in terms of this theory.
4. Explain the following terms as applied to the gaseous state. Compressibility, diffusability, and expansionability.
5. Explain the term "partial pressure". State and illustrate Dalton's law of partial pressures.
6. (a) What is the cause of gas pressure? How does temperature effect gas pressure and why?
(b) Suggest a suitable explanation for the fact that gases do not settle at the bottom of container.
7. What is an ideal gas? Why real gases are not ideal? What explanation can you give for the deviations of real gases from the ideal behaviour?
8. Compare the structure of solids, liquids and gases with regard to freedom of motion of their molecules.

9. What is meant by the phrase "intermolecular forces"?
 10. What feature characterises the equilibrium as being dynamic in the case of a vapour in equilibrium with its liquid?
 11. In terms of the kinetic-molecular theory, explain the cooling effect of evaporation.
 12. How are vapour pressures and intermolecular forces in liquids related?
 13. Define the term "boiling point". Why is the boiling point of a liquid lowered by reducing the external pressure?
 14. "Boiling point" is often distinguished from "normal boiling point". Explain what is meant by the two terms?
 15. What is the origin of the van der Waal's force?
 16. Methane (CH_4), ammonia (NH_3) and water (H_2O) have similar molecular weights. Yet methane has boiling point of 111.5°C , ammonia 239.6°C and water 373°C . What does this suggest with respect to the polar character and intermolecular attraction for each of the three compounds?
 17. How do crystalline solids and amorphous solids differ with regards to internal structure?
 18. Relate the magnitude of the melting point of a solid to the mutual attractive forces between its building units.
 19. Contrast crystalline and amorphous solids with regards to melting points.
 20. Explain in terms of internal structure the high melting point (and hardness) of diamond.
 21. Arrange the following solids in order of the increasing strengths of attractive forces: Ice (m.pt. 273°C) sodium fluoride (m.pt. 1272°C), naphthalene (m.pt. 353°C).
 22. (a) Define and explain the terms: surface tension and viscosity of liquids.
(b) Write a note on van der Waal's equation of state.
- (B) Objective Type :
23. Point out the correct statements in each of the following :
 - (a) Pressure depends upon the number of molecules and temperature.
 - (b) The molecules of real gases have both volume and mutual attraction.
 - (c) At normal temperatures and pressures, most gases behave nearly as ideal gases.
 - (d) With constant pressure, the volume of a gas is directly proportional to temperature.
 - (e) Gas molecules travel in straight lines between collisions.
 - (f) In a molecular collision, the kinetic energy of each of the colliding molecules have same value before and after the collisions.
 - (g) Most probable velocity is the maximum possible velocity for the molecules of a gas.
 - (h) At low pressures the molecules of a gas are moving more slowly than at high pressures.
 - (i) Each gas in a mixture exerts its pressure independently of the other gas present.

- (j) According to Charle's law, at absolute zero the volume of an ideal gas is zero.
- (k) The most probable kinetic energy of the molecules in a gas increases as the temperature is increased.
- (l) The rate of diffusion of a gas is inversely proportional to its density.
- (m) Thermal motion of molecules ceases at absolute zero.
- (n) The kinetic energy of a gas is directly proportional to the absolute temperature and is independent of the nature or pressure of the gas.
- (o) Real gases approximate to ideal behaviour only if the temperature is low and pressure is high.
- (p) Gases deviate from ideal behaviour at high pressure because intermolecular interactions become appreciable.

24. Fill in the blanks in the following statements :

- (a) The absolute temperature of a gas is a measure of the average.....
.....of all the molecules.
- (b) In an ideal gas equation $PV = nRT$, the gas constant R has the dimensions of.....
- (c) The time taken by a certain volume of hydrogen to diffuse through a small hole is.....than the time taken by equal volume of oxygen to diffuse under identical conditions.
- (d) The volume occupied by 1 mole of a gas at 237K and 760 cm Hg pressure is.....litres.
- (e) At boiling point, vapour pressure of a liquid become equal topressure.
- (f) A mixture of 2 moles of CH_4 and 1 mole of CO_2 occupies.....
litres at STP.
- (g) The pressure exerted by a gas in a container is due to.....of the gas molecules with the wall.
- (h) Gases occupy larger volumes than solids and liquids because.....
.....between molecules are low.
- (i) The gas molecules are in continuous random motion, inspite of the large number of collisions amongst them. It is because during collisions.....occurs.
- (j) Boiling point of a liquid is.....by reducing the external pressure.

C) Problems :

25. The volume of a given mass of gas is 500 ml at 300 K and 742 mm pressure. What volume will it occupy under standard conditions ?

(Ans. 267 ml)

26. Calculate the mass of dry hydrogen in 500 ml of moist hydrogen gas collected over water at 300 K and 740 mm. (Vapour pressure of water at 300 K is 21.1 mm, density of hydrogen at STP is 0.08987 g/l).

(Ans. 0.0392 g)

27. Calculate the relative rates of diffusion of CO_2 and H_2 (At. mass of C=12; O=16; H=1).

(Ans. 1 : 4. 67)

28. A 260 ml flask contained CO_2 at 500 mm. Hg. Another 450 ml flask contained oxygen at 950 mm Hg. The contents of the two flasks were mixed by

opening a stop-cock connecting them. Assuming that all operations were carried out at a uniform constant temperature, calculate the final total pressure of the resulting mixture. Neglect the volume of the stop-cock. (Ans. 789 mm Hg)

29. A pressure cooker contains boiling water and the gaseous pressure on the surface of water is approximately 2 atmospheres. State whether the boiling point of water in cooker is higher or lower than the normal boiling point.

30. Time of diffusion of same volume of oxygen and chlorine under similar conditions are 25 sec and 37.5 sec respectively. If the relative density of oxygen is 16, calculate that of chlorine. (Ans. 36.0)

31. 360 ml of a gas A diffuse through a porous vessel in 30 minutes. 120 ml of sulphur dioxide require 20 minutes to diffuse through the same vessel under identical conditions. The density of sulphur dioxide is 32. Calculate the density of gas A. (Ans. 16.0)



Chemical Energetics

6.1. INTRODUCTION

Energy is the capacity of a body for doing work. Many different forms of energy are recognized such as kinetic, potential, mechanical, electrical, light, heat, chemical, etc. Even matter itself is a form of energy. Chemical process, such as combustion (*i.e.* burning of coal, candle, etc. in excess of air), solution, dilution, neutralisation, atomisation and hydrogenation are invariably associated with a corresponding energy change. *A study of this energy change of a chemical change is called chemical energetics.*

In its simplest form, a study of the energy changes associated with chemical processes is concerned mainly with the evolution or absorption of heat, and is generally known as *thermochemistry*.

6.2. INTERNAL ENERGY

Every chemical system has internal energy, E , which is a function of the temperature, the chemical nature of the substance, and at times the pressure and volume of the system. The magnitude of the internal energy in a given system of molecules is determined by the kinetic, rotational and vibrational movement of the molecules and their component atoms as well as by the way in which the molecules are put together and the nature of the individual atoms. It is impossible to determine the absolute value of the internal energy of a system. Fortunately, we are concerned only with the changes in internal energy accompanying a chemical or physical change. This change in internal energy accompanying a chemical or physical change is represented by ΔE . If E_2 is the internal energy of the system in the final state and E_1 is the initial internal energy of the system (*i.e.*, before change), then

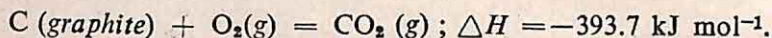
$$\Delta E = E_2 - E_1$$

6.3. ENTHALPY

A chemical reaction carried out at constant pressure (say, atmospheric) is accompanied by some energy change, which most obviously, involves the evolution or absorption of heat. For example, when carbon burns in oxygen, the reaction is represented.



At the same time energy equivalent of 393.7 kJ is released. The reaction is said to be exothermic (heat given out) and is generally written ;



where ΔH refers to change in enthalpy (sometimes known as change in heat content). The term **change in enthalpy** of a system is thus defined as "*total energy change at constant pressure and temperature*". Now, a reaction carried out at constant pressure generally involves a change in volume. So, enthalpy change is equal to change in internal energy plus work done during expansion against the pressure (i.e., product of pressure, P and volume change, ΔV).

$$\begin{aligned}\Delta H &= \Delta E + \text{Work done} \\ \therefore &= \Delta E + P\Delta V\end{aligned}$$

The work done during a chemical reaction at constant pressure depends upon the change of volume which occurs. If there is an increase in volume, the system has to do work against the constant pressure, and consequently, the change in enthalpy is less than the internal energy change by an amount equal to this work. If the system contracts in volume, work is done by the surroundings and the enthalpy change is greater than the internal energy change. When no change in volume occurs, the enthalpy change equals the internal energy change. Thus, *enthalpy change at constant volume is equal to change in internal energy*.

6.4. EXOTHERMIC AND ENDOTHERMIC REACTIONS

A reaction giving out heat to the surroundings is said to be **exothermic**. On the other hand, reaction absorbing heat from the surroundings is called **endothermic**. The heat changes are generally measured in Joule (J), which is the work done when the point of application of a force of 1 Newton (N) moves through 1 metre in the direction of force. Since the Newton is the force which produces an acceleration of 1 metre per second squared when it acts on a mass of 1 kilogramme, then

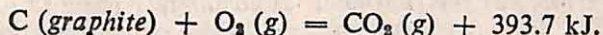
$$1 \text{ J} = 1 \times \text{N} \times \text{m} = 1 \times \text{Kg} \times \text{m}^2 \times \text{s}^{-2}$$

Multiples of the Joule in common use are the kilo Joule (kJ.).

$$1 \text{ kJ} = 1000 \text{ J}.$$

The heat changes associated with a reaction is conveniently written as a part of the ordinary chemical equation for the

reaction. Thus,



These equations mean that 393.7 kJ of heat is evolved when 1 mole of carbon reacts with 1 mole of oxygen.

An evolution of heat to the surroundings means that the system as a whole loses heat to the surroundings and, therefore, products possess a lower energy content. That is why ΔH is

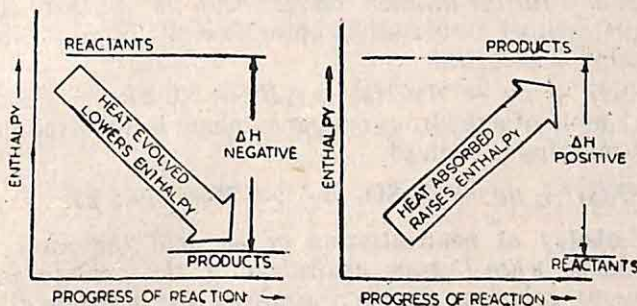


Fig. 6.1. Illustration of sign convention for enthalpy change (ΔH).

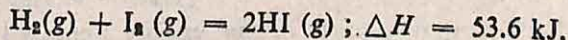
written negative for an exothermic reaction and positive for an endothermic reaction. It may be illustrated graphically as in Fig. 6.1.

6.5. ENTHALPY CHANGES IN DIFFERENT TYPE OF REACTIONS

1. Enthalpy of reaction is the difference between the enthalpies of the products and the reactants when the number of moles of reactants indicated by the chemical equation have completely reacted. For example, the reaction,

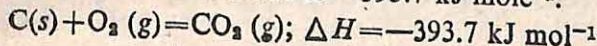


indicates that when 1 mole of solid carbon combines with 1 mole of gaseous oxygen to produce 1 mole gaseous carbon dioxide, the enthalpy of the system decreases by 393.7 kJ. Hence, the enthalpy of above reactions is -393.7 kJ . Similarly, the thermochemical reaction.

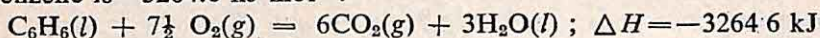


implies that when 1 mole of gaseous hydrogen combines with 1 mole of gaseous oxygen to produce 2 moles of gaseous hydrogen iodide, the enthalpy of the system increases by 53.6 kJ. Hence, enthalpy of this reaction is $+53.6 \text{ kJ}$.

2. Enthalpy of formation is the value of enthalpy change when 1 mole of the compound is formed from its elements in their commonly occurring (or standard) states. For example, enthalpy of formation of carbon dioxide is $-393.7 \text{ kJ mole}^{-1}$.



3. Enthalpy of combustion of a compound is the change in enthalpy when 1 mole of the substance is completely burnt in excess of oxygen or air. For example, the enthalpy of combustion of benzene is $-3264.6 \text{ kJ mol}^{-1}$.

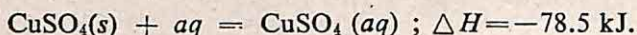


Since combustion reactions are always exothermic, so, enthalpy of combustion is always negative.

4. Enthalpy of solution of a substance is the change in enthalpy when 1 mole of the substance is dissolved in so much solvent that any further dilution brings about no enthalpy change. For example, when 1 mole sodium chloride is dissolved in water 5.0 kJ of enthalpy is absorbed.



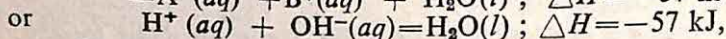
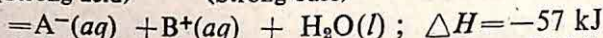
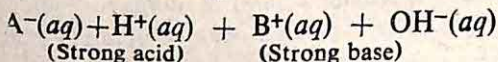
But when 1 mole of anhydrous copper sulphate is dissolved in water 78.5 kJ of enthalpy is evolved.



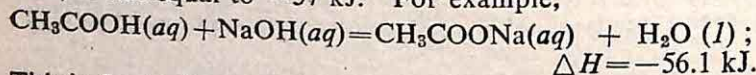
5. Enthalpy of neutralisation of an acid (or base) is the enthalpy change when 1 gram equivalent of the acid (or base) in dilute aqueous solution form is neutralised by a dilute alkali (or acid). For example, the enthalpy of neutralisation of HCl by NaOH is -57 kJ .



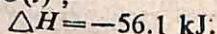
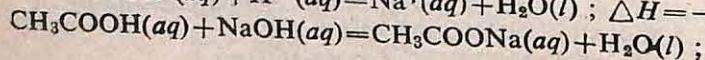
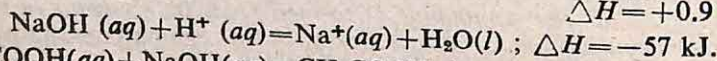
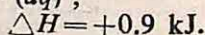
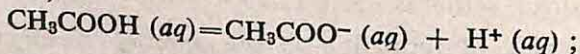
The enthalpy of neutralisation of all strong acids (HCl, H_2SO_4 , HNO_3 , H_3PO_4 , etc.) by strong base (NaOH, KOH, etc.) and vice versa is always found to be -57 kJ . This is because the enthalpy of neutralisation is in fact the enthalpy of formation of water from hydrogen ions (of acid) and hydroxyl ions (of base); while the other ions of the strong acid and base remains unaltered. Thus,



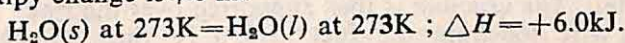
However, the enthalpy of neutralisation of a weak acid (or base) is not equal to -57 kJ . For example,



This is due to the fact that a part of the energy liberated during neutralisation is used up in causing complete ionisation of acetic acid, which is a weak acid. Thus, in the above reaction the difference $-56.1 - (-57) = +0.9 \text{ kJ}$ is heat of ionisation of acetic acid i.e.,

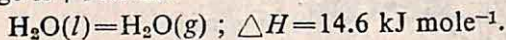


6. Enthalpy of fusion of a substance is the change in enthalpy accompanying the change of 1 mole of substance from the solid state to the liquid state at its melting point. Thus, when 1 mole of ice (solid water) changes into water at its melting point (273K), the enthalpy change is +6 kJ.



Since fusion reaction are always endothermic, so *enthalpy of fusion is always positive*. It may be pointed out that value of enthalpies of fusion of solids depend on the nature of their intermolecular forces. Consequently, enthalpy of fusion is low in case of molecular solids (e.g., $\text{CCl}_4 = +2.5\text{ kJ mol}^{-1}$; $\text{H}_2\text{S} = 2.5\text{ kJ mol}^{-1}$) and high in case of ionic solids (i.e., $\text{NaCl} = +29.0\text{ kJ mol}^{-1}$),

7. Enthalpy of vaporisation of a liquid is the change in enthalpy accompanying the conversion of 1 mole of liquid into vapours at its normal boiling point. For example, when 1 mole of water changes into vapour at its boiling point (373K), the enthalpy change is +14.6 kJ.



It may be pointed here that value of enthalpy of vaporisation depends on strength of intermolecular cohesive forces. Consequently, enthalpy of vaporisation of water (having hydrogen bonding and dipole-dipole interaction) is higher than that of hydrogen sulphide (+13.8 kJ mol⁻¹) since the molecules of latter are bonded only by weak van der Waal's forces.

8. Enthalpy of sublimation of a substance is the enthalpy change accompanying the conversion of 1 mole of solid directly into vapour, at a temperature below its melting point. For example, when 1 mole of iodine sublimates to give iodine vapour the enthalpy change is +62.4 kJ.



It may be pointed here that sublimation is nothing but fusion and vaporisation carried out in one step. So,

$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vaporisation}}$$

6.6. DETERMINATION OF ENTHALPY OF REACTION

The measurement of enthalpy changes in reactions is termed **calorimetry**. Measurement of enthalpy change at constant volume (ΔE) is usually carried out in a **bomb calorimeter** (see Fig. 6.2). It consists of strong cylindrical stainless steel bomb in which the combustion of fuel is made to take place. The bomb has a lid which can be screwed to the body of bomb to make a perfect gas-tight seal. The lid is provided with two stainless steel electrodes and an oxygen inlet valve. To one of the electrodes, a small ring is attached. In this ring a nickel or stainless steel crucible can be supported. The bomb is placed in a copper calorimeter, which is surrounded by an air-jacket and water-jacket to prevent losses due

to radiation. The calorimeter is provided with an electrically operated stirrer and Beckmann's thermometer, which can read accurately temperature difference up to $1/100$ th of a degree.

A known mass (about 0.5 to 1.0 g) of the given fuel is taken in clean crucible. The crucible is then supported over the ring. A fine magnesium wire touching the fuel sample is then stretched across the electrodes. The bomb lid is tightly screwed and filled with oxygen to 25 atmospheric pressure. The bomb is then lowered

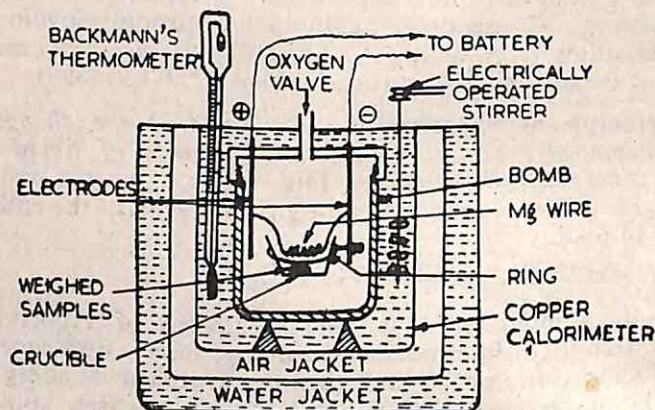


Fig. 6.2. Bomb calorimeter.

into copper calorimeter containing a known mass of water. The stirrer is worked and initial temperature of the water is noted. The electrodes are then connected to 6-volt battery and circuit completed. The sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained is recorded.

Knowing the rise in temperature of a water and the heat capacity of calorimeter, etc. the amount of heat evolved can be calculated. From that heat of reaction at constant volume (ΔE) can thus be calculated.

6.7. DETERMINATION OF ENTHALPY OF NEUTRALISATION

For the determination of enthalpy of neutralisation of an acid, a thermos or vacuum flask of 1 litre capacity may be employed as a calorimeter. The thermal capacity (in grams of water) of flask is first measured by adding 100 ml of warm water at about 330K to it and measuring the fall in temperature of the water. Then,

Thermal capacity (C) \times Rise in temperature = 100 \times fall in temperature of water.

The flask is then emptied and 100 ml of 1N solution of alkali is placed in it and its temperature is recorded (T_1). 100 ml of 1N solution of given acid, at a measured temperature (T_2) is

then quickly added. The mixture is stirred and the highest temperature (T_3) reached by the mixture is recorded.

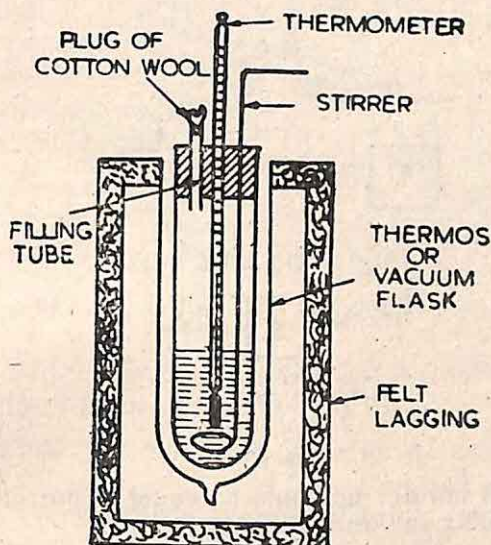


Fig. 6.3. Use of a vacuum flask for measurement of enthalpy of neutralisation.

Taking the densities of the alkali, acid and salt solution formed as unity, the heat evolved by the neutralisation process is given by :

$$\begin{aligned} & (100+C)(T_3-T_1) + 100(T_3-T_2) \text{ cal.} \\ & = 4.2 [(100+C)(T_3-T_1) + 100(T_3-T_2)] \text{ J} \\ & = x \text{ J (say).} \end{aligned}$$

\therefore Enthalpy of neutralisation (i.e., for 1000 ml of 1N solution).

$$\begin{aligned} & = -\frac{1000 \times x}{100} \\ & = -10 \times x \text{ J.} \end{aligned}$$

6.8. HESS'S LAW OF CONSTANT HEAT SUMMATION

This law was first deduced by Hess, a Russian chemist, in 1840 and states that "the enthalpy change in a chemical process is the same whether it take place in one step or in several steps, since the overall change depends only on the properties of the initial and final substances. It is direct consequence of the law of energy. Thus, the enthalpy change in a reaction A to C is the same whether the reaction takes place in one stage as :



or in two stages as :

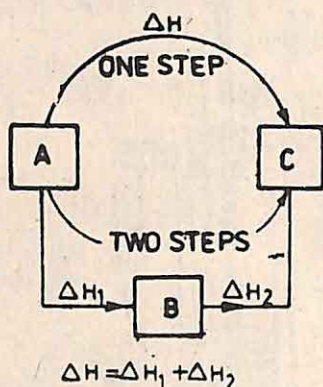


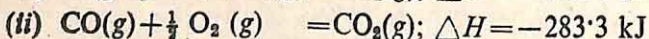
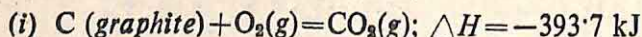
Fig. 6.4.

If the Hess's law did not hold it would be possible to obtain energy without doing any work. Suppose

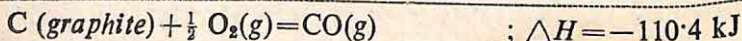
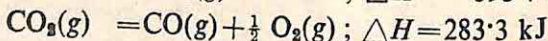
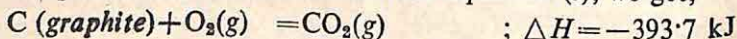
$$\Delta H > \Delta H_1 + \Delta H_2$$

so in going from A to C by the *first* path and then back to A by the second path (i.e., $C \rightarrow B \rightarrow A$, would yield $\Delta H - (\Delta H_1 + \Delta H_2)$ kJ of heat from nowhere. This is contrary to all scientific experience. Hence, ΔH must be equal to $\Delta H_1 + \Delta H_2$.

Applications. Using Hess's law it is possible to determine indirectly the enthalpy change in a reaction, even though it may be impossible to measure such enthalpy of reaction experimentally. For example, it is impossible to measure accurately the heat liberated when C burns to CO, because the oxidation cannot be stopped exactly at the CO stage. However, it is possible to measure accurately the heat liberated when C burns to CO_2 ($\Delta H = 393.7 \text{ kJ mol}^{-1}$) and also the heat liberated when CO burns to CO_2 ($\Delta H = 283.3 \text{ kJ mol}^{-1}$). The enthalpy change for burning of C to CO is determined by treating algebraically these experimentally determined thermochemical equations.



If equation (ii) is subtracted from equation (i), we get,

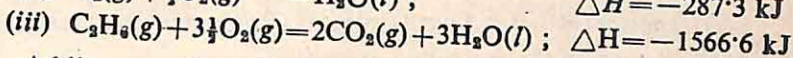
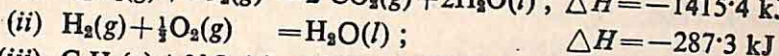
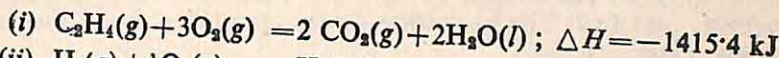


Thus, enthalpy of formation of CO (g) is -110.4 kJ .

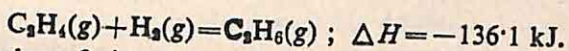
Hence, Hess's law enables thermochemical equations to be added and subtracted.

Example 6.1. Calculate the enthalpy of the reaction: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ at 298K given that the enthalpies of combustion of ethylene, hydrogen and ethane are -1415.4 , -287.3 , and -1566.6 kJ respectively.

The thermo-chemical equations for the combustion of ethylene, hydrogen and ethane are :

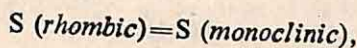


Adding equations (i) and (ii) and subtracting equation (iii), we get

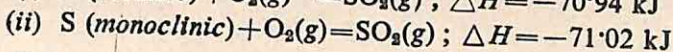
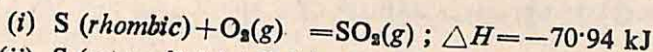


Hence, enthalpy of given reaction is -136.1 kJ.

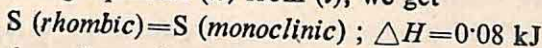
Example 6.2. Calculate the enthalpy of transition for the reaction,



given



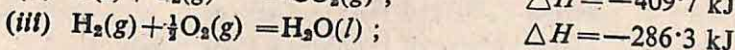
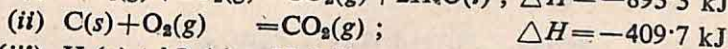
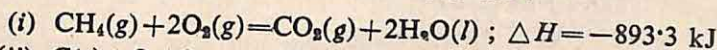
Subtracting equation (ii) from (i), we get



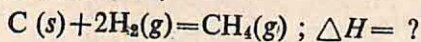
Hence, enthalpy of reaction is 0.08 kJ or 80 J.

Example 6.3. Calculate the enthalpy of formation of methane (CH_4), if the enthalpy of combustion of methane is -893.3 kJ mol⁻¹ and the enthalpies of formation of carbon dioxide and water are -409.7 and -286.3 kJ mol⁻¹, respectively.

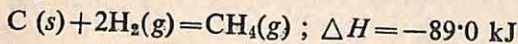
The thermochemical equations for the combustion of methane and formation of carbon dioxide and water are :



The formation of methane may be written in a thermo-chemical form as ;



Adding equation (ii) to 2 times equation (iii) and subtracting (i), then we get



Hence, enthalpy of formation of $CH_4 = -89.0$ kJ mol⁻¹.

6.9. BOND ENTHALPY

The enthalpy of reaction resulting from the breaking of a chemical bond in a gaseous molecule to form the respective gaseous molecular fragments is known as the bond dissociation enthalpy.

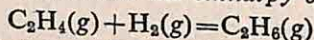
Bond enthalpy can be used to calculate the enthalpy of a reaction by assuming the reaction to consist of two steps.

(i) The decomposition of the reactants into molecular fragments, and (ii) The formation of the products from the fragments. Thus,

$$\Delta H(\text{reaction}) = -\text{Bond enthalpies of (Products—Reactants)}$$

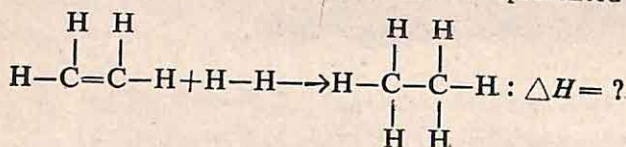
This is illustrated in the following examples.

Example 6.4. Determine the enthalpy of hydrogenation,



given the bond enthalpies of $\text{H}-\text{H}$, $\text{C}=\text{C}$, $\text{C}-\text{C}$, $\text{C}-\text{H}$ bonds as 435.7, 614.8, 347.5, 413.2 kJ respectively.

The hydrogenation of ethylene can be represented as :

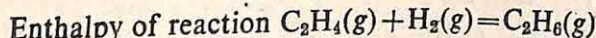


Bond enthalpies of reactants,

$$\begin{aligned} &= \text{Bond enthalpies of } (4 \times \text{C}-\text{H} + \text{C}=\text{C} + \text{H}-\text{H}) \\ &= (4 \times 413.2 + 614.8 + 435.7) \text{ kJ} \\ &= (1652.8 + 614.8 + 435.7) \text{ kJ} \\ &= 2703.3 \text{ kJ} \end{aligned}$$

Similarly, bond enthalpies of product,

$$\begin{aligned} &= \text{Bond Enthalpies of } (6 \times \text{C}-\text{H} + \text{C}-\text{C}) \\ &= (6 \times 413.2 + 347.5) \text{ kJ} \\ &= (2479.2 + 347.5) \text{ kJ} \\ &= 2826.7 \text{ kJ} \end{aligned}$$



$$\begin{aligned} &= -(\text{Bond enthalpies of Products—Reactants}) \\ &= (-2826.7 + 2703.3) \text{ kJ} \\ &= -123.4 \text{ kJ} \end{aligned}$$

6.10. CALORIFIC VALUES OF FOOD AND FUELS

All machines, locomotives, automobiles and industrial plants need energy for their working. Even human body is a machine needing energy for its working. While coal, diesel, petrol, natural gas, etc., serve as the principle sources of energy for industry ;

the food we eat serves as a source of energy to human body. These, therefore, are known as *fuels*. The oxidation (*i.e.*, combustion) of these fuels releases chemical energy. Food, which is a fuel for human body, also releases energy on its oxidation during the process of digestion, and keeps the body warm. Carbon present in food is oxidised to carbon dioxide, hydrogen to water which are pushed out when we inhale. Nitrogen is converted mostly to urea, which is eliminated in urine.

The energy released due to oxidation of any fuel is measured in terms of **calorific value**. It is defined as *the quantity of heat evolved when 1 gram of fuel is burnt completely in oxygen*. Calorific values are generally expressed in kilocalories per gram of the fuel. The choice of gram in place of mole is on account of the fact that molecular mass of a fuel is invariably not well-defined.

The calorific value of a fuel can be determined by using a bomb calorimeter. A known mass of the fuel is burnt in excess of oxygen and the change in temperature is noted and the amount of energy released is calculated.

Different food stuffs possess different calorific values. Fats and carbohydrates are the main source of heat in foods. The calorific value of protein is low (about 4 kcal g⁻¹). Calorific value of important foods are given below.

Bread = 2.7 kcal g ⁻¹ ;	Rice = 4.00 kcal g ⁻¹
Milk = 0.72 kcal g ⁻¹ ;	Sugar = 4.13 kcal g ⁻²
Butter = 8.04 kcal g ⁻¹ ;	Dates = 3.58 kcal g ⁻¹
Cheese = 4.73 kcal g ⁻¹ ;	Egg, Yolk = 3.40 kcal g ⁻²
Meat = 2.73 kcal g ⁻¹ ;	Egg, (white) = 0.50 kcal g ⁻¹
Fish = 1.2 kcal g ⁻¹ ;	Potatoes = 0.88 kcal g ⁻¹

Balanced diet. To maintain proper health and growth we need food which contains all the food essentials—carbohydrates, oils and fats, proteins, vitamins and mineral salts. A balanced diet is one which contains suitable quantities of these food essentials. A balanced diet contains approximately, carbohydrates, fats, and proteins in the ratio 4 : 1 : 1. The average requirement of energy is about 3,500 calories for a normal youngman.

QUESTIONS

(A) Essay Type :

1. What do you understand by the terms : (a) Internal energy and (b) Enthalpy of a system ? What is the relationship between ΔE and ΔH ?
2. State Hess's Law. How does it enable us to predict the enthalpy of a reaction ?
3. Explain the terms : enthalpy of reaction, enthalpy of formation, enthalpy of combustion, enthalpy of solution and enthalpy of neutralisation. Why is the enthalpy of neutralisation of a strong acid and a strong base constant ?
4. Explain the terms : enthalpy of fusion, enthalpy of vaporisation and enthalpy of sublimation. How are they interrelated ?

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5. How is a bomb calorimeter used for the determination of enthalpy of combustion?

6. What is bond enthalpy? How can it be used to predict enthalpy of a reaction?

7. What is meant by calorific value of a fuel? What is the function of food in the body?

(B) Objective Type :

8. Fill in the blanks :

- In an endothermic reaction the enthalpy of the products is..... than that of reactants.
- In an exothermic reaction the enthalpy of the reactants is..... than that of products.
- In an exothermic reaction ΔH is..... and in an endothermic reaction ΔH is.....
- Combustion reaction is always..... and ΔH for this reaction is.....
- Enthalpy of fusion is always.....
- Enthalpy of sublimation is always.....
- The enthalpy of formation of a substance from its elements is the.....
- Enthalpy of neutralisation of all strong acids and bases is.....

(C) Problems :

9. Calculate the enthalpy of formation of benzene from acetylene.



if (i) $\text{C}_6\text{H}_6(\text{l}) + 7\frac{1}{2}\text{O}_2(\text{g}) = 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \quad ; \quad \Delta H = -3345.5 \text{ kJ}$

(ii) $\text{C}_2\text{H}_2(\text{g}) + 2\frac{1}{2}\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \quad ; \quad \Delta H = -1297 \text{ kJ}$
(Ans. $-546.5 \text{ kJ mol}^{-1}$)

10. Calculate the enthalpy of formation of liquid ethanol at 298K, given the following enthalpy of reaction at the same temperature.

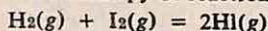
(i) $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) = 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \quad ; \quad \Delta H = -1386 \text{ kJ}$

(ii) $\text{C}(\text{s}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g}) \quad ; \quad \Delta H = -393.2 \text{ kJ}$

(iii) $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l}) \quad ; \quad \Delta H = -286.3 \text{ kJ}$

(Ans. $277.3 \text{ kJ mol}^{-1}$)

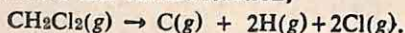
11. Calculate the enthalpy of reaction,



if bond enthalpy of H—H, I—I, H—I bonds are 433, 151, 299 kJ respectively.

(Ans. -14.0 kJ)

12. Calculate ΔH for the reaction,



if bond enthalpy of C—H and C—Cl bonds are 415.0 and 326.0 kJ respectively.

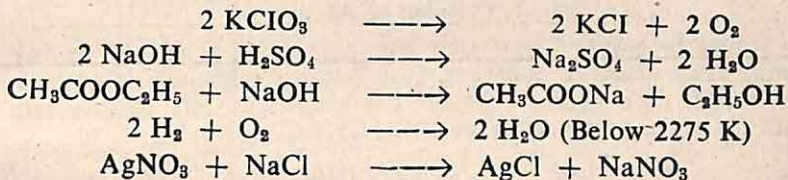
(Ans. -1482 kJ)



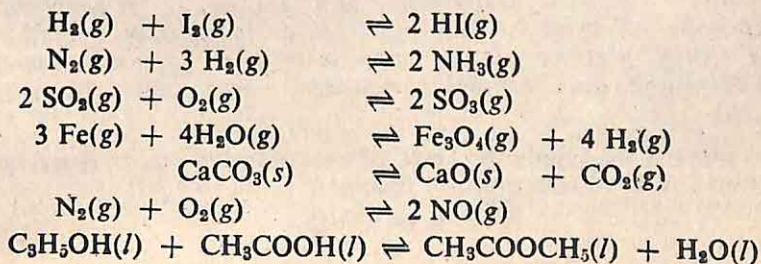
Chemical Equilibrium

7.1. REVERSIBLE AND IRREVERSIBLE REACTIONS

All chemical reactions are competitive process and can take place in both directions. The extent to which this happens, however, varies from reaction to reaction. In many cases, the extent of the reverse reaction is negligible so that they can be considered as proceeding completely in one direction. Examples are :



Such reactions which proceed almost completely in one direction are said to be **irreversible**. However, when the forward and reverse reactions both occur to an appreciable extent, the process is said to be **balanced** or **reversible**, generally represented by \rightleftharpoons . As the forward products are formed, they tend to recombine, regenerating the reactants, i.e., the reaction does not proceed completely in either direction. After a sufficient length of time all reversible reactions reach a "dynamic chemical equilibrium" in which the two opposing changes occur simultaneously at the same rate. When this condition is reached, the composition no longer changes with time at a fixed temperature and pressure. Examples are :



If several tubes containing equimolecular quantities of hydrogen and iodine, are heated to 637K and the contents are analysed at various intervals, it is found that chemical equilibrium is attained when 80 percent of the gases have been converted to hydrogen iodide. Conversely, if tubes containing pure hydrogen iodide are similarly treated, it is found that chemical equilibrium is established when 20 percent of the gas has been decomposed (Fig. 7.1).

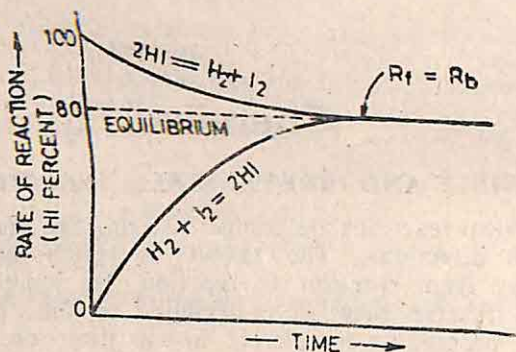
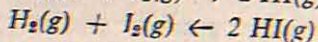
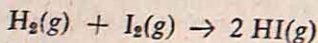


Fig 7.1. Chemical equilibrium.

It may be pointed here that the composition of the equilibrium-mixture remains constant, not because chemical reactions are no longer taking place between the molecules, but because the speeds of the forward and backward reactions, namely,

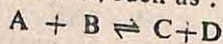


have become the same.

7.2. LAW OF MASS ACTION—EFFECT OF CONCENTRATION ON EQUILIBRIUM

The position of equilibrium of a reversible reaction and speed with which it is obtained are affected by the concentration of the substances present. The relationship between these quantities was deduced by Guldberg and Waage (1867) and described as the 'Law of Mass Action'. According to it "at constant temperature the rate of a reaction is proportional to the active masses of each of the reactants." The term "active mass" of a substance is its concentration in gram molecules per litre (in case of components of a solution) or as partial pressure (of the components of a gaseous system). Concentrations are normally expressed in square brackets, e.g. [A].

Suppose we apply the law of mass action to a reversible reaction at a fixed temperature, such as :



This equation states that substances A and B react to form substances C and D, and that C and D react under the same conditions to form the original reactants A and B.

By the law of mass action, the rate of forward reaction is proportional to the product of the concentrations of A and B i.e.,

$$R_f = k_1 \times [A] \times [B]$$

Similarly, $R_b = k_2 \times [C] \times [D]$

where k_1^* and k_2 are called respectively the velocity constant of the forward and backward reactions.

At equilibrium :

$$R_f = R_b$$

∴

$$k_1 [A] [B] = k_2 [C] [D]$$

or

$$\frac{k_1}{k_2} = K_c = \frac{[C] [D]}{[A] [B]}$$

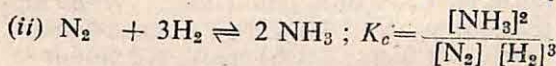
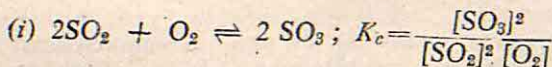
K_c is called the *equilibrium constant* for the reaction. Just as k_1 and k_2 are proportionally constant specific for each reaction at a definite temperature, K_c is likewise a constant specific to this system in equilibrium at a given temperature. By convention it is always quoted as the product of active masses of the products of the forward reaction divided by the product of the active masses of the forward reactants.

When several molecules of each reactant and/or product are involved, a modified form of the law of mass action is used. The rate of a reaction is directly proportional to the product of the active masses of the reacting substances raised to the power of the number of molecules reacting, as expressed by the equation. Thus, for the reaction



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Examples are as following :



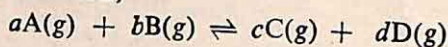
This is the mathematical expression of the law of mass action which may be restated as follows. "When a reversible reaction has

*The increase in reaction rate that accompanies an increase in concentration of reacting substance is readily explained in terms of kinetic-molecular theory. By increasing the concentration of any or all of the reacting substances, the chances of collision between molecules are increased due to the presence of a greater number of molecules per unit volume. More collisions per unit time means a greater reaction rate. The concentration of a substance when expressed in moles/litre provides a direct measure of the number of molecules per unit space.

attained equilibrium at a given temperature, the product of the molar concentrations of the substances to the right of the arrow of the equation, divided by the molar concentrations of the substances to the left, each concentration raised to the power equal to the number of molecules of each substance appearing in the equation, is a constant".

Consequently, if the equilibrium lies well over to the side of the forward products at the given temperature, K_c will be large; whereas if it lies well over to the side of the forward reactants, K_c will be small.

For a reversible homogeneous reaction between gases, the concentrations are expressed as partial pressures and the equilibrium constant for the reaction,

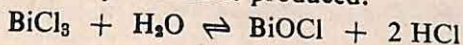


possess two forms of equilibrium constant one referred to concentrations (K_c) and the other to partial pressures (K_p).

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad ; \quad K_p = \frac{[P_c]^c [P_d]^d}{(P_a)^a (P_b)^b}$$

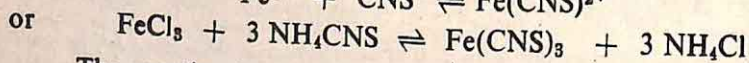
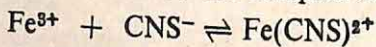
where the 'P' terms are partial pressures.

Illustration of law of mass action. The fact that the position of equilibrium depends upon the concentration of substances present can be shown by adding water to a concentrated aqueous solution of bismuth trichloride. As the solution is diluted, a white turbidity of bismuth oxychloride is produced.



Addition of more water yields a white precipitate. Now, if a little concentrated hydrochloric acid is added to the mixture, the precipitate dissolves showing that the [hydrolysis reaction has been reversed as indicated by the lower arrow in the above equation. The equilibrium can be driven to right again by the addition of more water.

The application of law of mass action can be demonstrated by the reaction between ferric ions and thiocyanate ions. When an aqueous solution of a thiocyanate (like NH_4CNS) is added to an aqueous solution of a ferric salt (e.g., $FeCl_3$) pale red colour is produced due to the formation of the complex cation, $Fe(CNS)^{2+}$



The reaction is reversible, hence if more ferric or thiocyanate ions are added to this mixture, the red colour of mixture becomes more intense by driving the equilibrium towards the right. On the other hand, if a concentrated solution of a salt, such as ammonium chloride, is added the colour of the mixture fades. This is due to the fact that the equilibrium has been forced to move to

left, thus decreasing the concentration of coloured complex, (see Fig. 7.2).

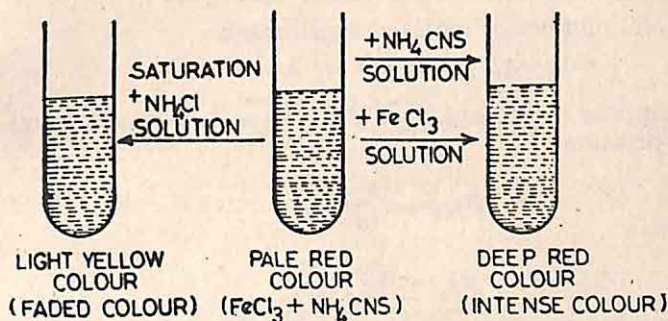
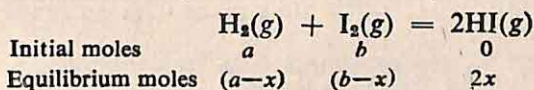


Fig. 7.2. Illustration of law of mass action.

7.3. FIRST-TYPE OF REACTIONS

Reactions in which there is no change in the number of molecules as a result of reaction are called "first type of reactions". In such a case, K_p and K_c are "identical" and subscription can be omitted. Let us apply law of mass action to some reactions.

(a) *Hydrogen iodide equilibrium.* Suppose a mixture of 'a' moles of hydrogen and 'b' moles of iodine, occupying a volume V , is brought to equilibrium point, and that 'x' moles of each have been converted to hydrogen iodide. So, the number of moles of hydrogen, iodine and hydrogen iodide at equilibrium, are $(a-x)$, $(b-x)$, and $2x$, respectively.



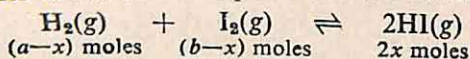
Hence, equilibrium molar concentrations $[\text{H}_2]$, $[\text{I}_2]$ and $[\text{HI}]$ are $(a-x)/V$, $(b-x)/V$ and $2x/V$ respectively.

$$\begin{aligned} \therefore K_c &= \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \\ &= \frac{\left(\frac{2x}{V}\right)^2}{\frac{(a-x)}{V} \times \frac{(b-x)}{V}} = \frac{4x^2}{(a-x)(b-x)} \end{aligned}$$

The expression does not include the term V , indicating that the equilibrium is independent of volume and, therefore, of pressure.

In a gaseous reaction, the equilibrium constant may be evaluated in terms of partial pressures. The moles of various

constituents of mixture at equilibrium are as follows :



∴ Total number of moles at equilibrium

$$= (a-x) + (b-x) + 2x = a + b.$$

Suppose the pressure of the system is P atmospheres. Then, partial pressure

$$p_{\text{H}_2} = \frac{(a-x)P}{(a+b)}$$

and

$$p_{\text{I}_2} = \frac{(b-x)P}{(a+b)}$$

and

$$p_{\text{HI}} = \frac{2x.P}{(a+b)}$$

$$K_p = \frac{(p_{\text{HI}})^2}{p_{\text{H}_2} \times p_{\text{I}_2}}$$

or

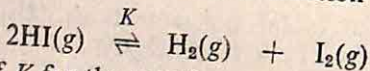
$$K_p = \frac{\left(\frac{2xp}{a+b}\right)^2}{\frac{(a-x)P}{(a+b)} \times \frac{(b-x)P}{(a+b)}}$$

i.e.,

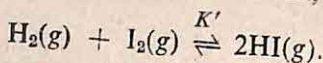
$$K_p = \frac{4x^2}{(a-x)(b-x)} = K_c.$$

As P is not present in this expression, the composition of the system at equilibrium is independent of the pressure. This is true to all reversible reactions which take place with no change in the number of molecules.

The value of K for the reverse reaction



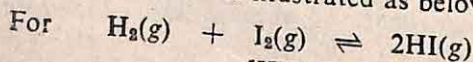
is reciprocal of K for the reaction;



In other words :

$$K = \frac{1}{K'}.$$

The unit of K in all first type of reactions is nil, i.e., K is dimensionless. This is illustrated as below :



$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(\text{mol/l})^2}{(\text{mol/l})(\text{mol/l})} = \text{nil}.$$

(b) *Formation of nitric oxide.* This was the basic reaction, which is the now obsolete Birkland-Eyde process for the manufacture of nitric acid from nitrogen. The equilibrium reaction is :

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}(\text{g})$$

Initial moles	a	b	0
Equilibrium moles	$(a-x)$	$(b-x)$	$2x$
Concentration (moles litre ⁻¹)	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$

Applying the law of mass action ; we get

$$K_p = K_c = \frac{[\text{NO}]^2}{[\text{N}_2] \times [\text{O}_2]} = \frac{\frac{(2x)^2}{V^2}}{\frac{(a-x)}{V} \cdot \frac{(b-x)}{V}} = \frac{4x^2}{(a-x) \cdot (b-x)}$$

(c) *Esterification of Ethyl Alcohol by Acetic Acid.* This is a reaction in solution and is represented by the equation.

$$\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$$

Initial moles	a	b	0	0
Equilibrium moles	$(a-x)$	$(b-x)$	x	x
Concentration (mol/l)	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

Let us start with 'a' moles of acid and 'b' moles of alcohol. Let 'x' moles each of ester and water are formed at equilibrium. If 'V' is the total volume of the solution mixture, then equilibrium molar concentrations are :

$$[\text{CH}_3\text{COOH}] = (a-x)/V ; [\text{C}_2\text{H}_5\text{OH}] = (b-x)/V ; [\text{CH}_3\text{COOC}_2\text{H}_5] = x/V ; [\text{H}_2\text{O}] = x/V.$$

Applying law of mass action, we get

$$K_c = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}] [\text{C}_2\text{H}_5\text{OH}]} = \frac{(x/V) \times (x/V)}{\frac{(a-x)}{V} \cdot \frac{(b-x)}{V}} = \frac{x^2}{(a-x)(b-x)}$$

Example 7.1. 10 moles of HI were produced by the interaction of 15 moles of H_2 and 5.2 moles of I_2 vapour at 717K. Calculate the equilibrium constant for the reaction : $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$.

For reaction :

	$\text{H}_2(\text{g})$	$+$	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
Initial moles	a		b		0
Equilibrium moles	$(a-x)$		$(b-x)$		$2x$
Concentration	$\frac{(a-x)}{V}$		$\frac{(b-x)}{V}$		$\frac{2x}{V}$

$$\therefore K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x/V)^2}{\frac{a-x}{V} \cdot \frac{b-x}{V}} = \frac{4x^2}{(a-x)(b-x)}$$

Here $a=15$; $b=5.2$; $2x=10$ or $x=5.0$

$$\therefore K_c = \frac{4(5)^2}{(15-5)(5.2-5)} = \frac{4 \times 25}{10 \times 0.2} = 50.0$$

Hence, the equilibrium constant of the reaction is 50.0.

Example 7.2. The equilibrium constant for the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ at 721K is found to be 64. If 6 moles of hydrogen are mixed with 3 moles of iodine in a one-litre vessel at this temperature, what will be the concentration of each of the three components when the equilibrium is attained?

For reaction :	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
Initial moles	6		3		0
Equilibrium moles	$(6-x)$		$(3-x)$		$2x$
Concentration (mole litre ⁻¹)	$\frac{(6-x)}{1}$		$\frac{(3-x)}{1}$		$\frac{2x}{1}$

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(6-x)(3-x)} = \frac{4x^2}{18-9x+x^2} = 64$$

$$\text{or } \frac{x^2}{18-9x+x^2} = 16$$

$$\text{or } x^2 = 16 \times 18 - 16 \times 9x + 16x^2$$

$$\text{or } 15x^2 - 144x + 288 = 0$$

$$\text{or } 5x^2 - 48x + 96 = 0$$

$$\begin{aligned} \text{or } x^* &= \frac{48 \pm \sqrt{(48)^2 - 4 \times 5 \times 96}}{2 \times 5} \\ &= \frac{48 \pm \sqrt{384}}{10} \\ &= \frac{48 \pm 19.75}{10} = 2.258 \text{ or } 0.942 \end{aligned}$$

Hence, composition of equilibrium mixture will be :

$$\text{H}_2 = 6 - 2.258 \text{ (or } 0.942) = 3.742 \text{ (or } 5.058) \text{ mole/litre.}$$

$$\text{I}_2 = 3 - 2.258 \text{ (or } 0.942) = 0.742 \text{ (or } 2.058) \text{ mole/litre.}$$

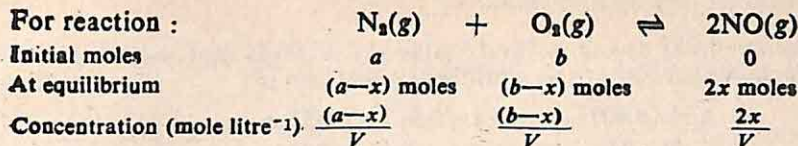
$$\text{HI} = 2 \times 2.258 \text{ (or } 0.942) = 4.516 \text{ (or } 1.884) \text{ mole/litre.}$$

Example 7.3. When a mixture of 1 mole of N_2 and 0.25 mole of oxygen is allowed to come to equilibrium at 3257 K, 0.125 mole of nitric oxide is formed. Calculate the equilibrium constant of the reaction.

*Roots of quadratic equation $ax^2 + bx + c = 0$ are

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

For reaction :

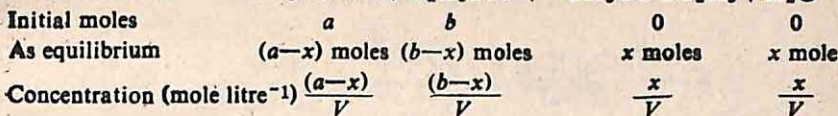


$$\begin{aligned}
 K_c &= \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x/V)^2}{\frac{(a-x)}{V} \frac{(b-x)}{V}} \\
 &= \frac{4x^2}{(a-x)(b-x)}
 \end{aligned}$$

 Substituting $a=1$, $b=0.25$; $2x=0.125$ or $x=0.0625$, we get

$$\begin{aligned}
 K_c &= \frac{4 \times (0.0625)^2}{(1-0.0625)(0.25-0.0625)} \\
 &= \frac{4 \times 0.0625 \times 0.0625}{0.9375 \times 0.1875} \\
 &= 0.267.
 \end{aligned}$$

Example 7.4. The equilibrium constant for the reaction $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ is 4.0. What will be the composition of the equilibrium mixture if 1 mole of acid is taken along with 8 moles of alcohol?

 For reaction : $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$


$$\begin{aligned}
 K_c &= \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} \\
 &= \frac{(x/V)(x/V)}{\frac{(a-x)}{V} \times \frac{(b-x)}{V}} \\
 &= \frac{x^2}{(a-x)(b-x)}
 \end{aligned}$$

 Substituting $a=1$; $b=8$; $K_c=4.0$, we get,

$$4 = \frac{x^2}{(1-x)(8-x)} = \frac{x^2}{8-9x+x^2}$$

or

$$x^2 = 32 - 36x + 4x^2$$

or

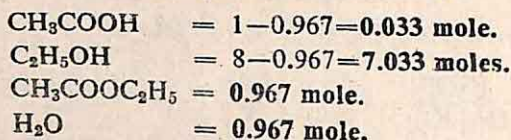
$$3x^2 - 36x + 32 = 0$$

or

$$x = \frac{36 \pm \sqrt{(36)^2 - 4 \times 3 \times 32}}{2 \times 3}$$

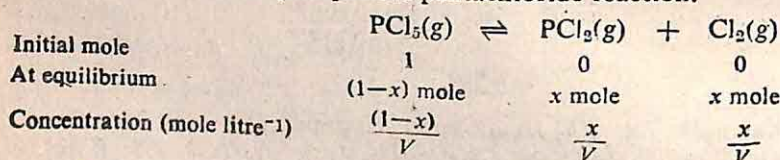
$$= \frac{36 \pm 30.2}{6} = 0.967 \text{ or } 11.03$$

whence $x=0.967$ as the second value of 11.03 is not admissible. Hence, composition of the equilibrium mixture is :



7.4. SECOND TYPE OF REACTIONS

Reaction in which number of molecules change as a result of reaction, are called "second type of reactions." The composition of such system at equilibrium depends upon the total pressure. Also K_c is not equal to K_p in such a case. This is illustrated by considering the dissociation of phosphorus pentachloride reaction.



Let us start with 1 mole of PCl_5 enclosed in a vessel of volume 'V' litres. Suppose 'x' mole of PCl_5 decomposes at the equilibrium to yield x mole each of PCl_3 and Cl_2 . Then,

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{(1-x)}{V}} = \frac{x^2}{(1-x)V}$$

The unit of K_c is litre⁻¹.

In order to calculate the value of K_p , we have total number of moles at equilibrium = $(1-x) + x + x = (1+x)$. Suppose the pressure of the system is P atmosphere. Then, partial pressures

$$p_{\text{PCl}_5} = \frac{(1-x)P}{(1+x)}$$

and

$$p_{\text{PCl}_3} = \frac{xP}{(1+x)}$$

and

$$p_{\text{Cl}_2} = \frac{xP}{(1+x)}$$

$$\therefore K_p = \frac{p_{\text{PCl}_3} \times p_{\text{Cl}_2}}{p_{\text{PCl}_5}} = \frac{\frac{xP}{(1+x)} \times \frac{xP}{(1+x)}}{\left[\frac{(1-x)P}{1+x} \right]} = \frac{x^2 P}{(1-x^2)}$$

The units of K_p in this case is atmosphere.

It can be seen that x (the degree of dissociation of PCl_5)

varies with pressure. If x is small, $(1-x^2)$ is approximately equal to 1.

$$\therefore K_p = x^2 P$$

or

$$x = \sqrt{\frac{K_p}{P}}$$

Thus, by increasing the total pressure, x is decreased.

Example 7.5. 2g molecules of PCl_5 are heated in a closed two-litre vessel. When the equilibrium is attained, the pentachloride is 40% dissociated into PCl_3 and Cl_2 . Calculate the equilibrium constant.

For reaction :

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial	a moles		0		0
At equilibrium	$(a-x)$ moles		x moles		x moles
Concentration (mole litre ⁻¹)	$\frac{(a-x)}{V}$		$\frac{x}{V}$		$\frac{x}{V}$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(x/V)(x/V)}{(a-x)/V} = \frac{x^2}{(a-x)V}$$

Substituting $a=2$; $V=2$ litres, $x=40\%$ of $2=0.4 \times 2=0.8$, we get

$$K_c = \frac{(0.8)^2}{(2-0.8) \times 2} = \frac{0.8 \times 0.8}{1.2 \times 2} = 0.267.$$

Example 7.6. Phosphorus pentachloride is 82% dissociated into phosphorus trichloride and chlorine, all gaseous, at 525 K and 1 atmosphere. Calculate the equilibrium constant of dissociations.

For the reaction :

	$\text{PCl}_5(\text{g})$	\rightleftharpoons	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial	1 mole		0		0
At equilibrium	$(1-x)$ mole		x mole		x mole
Partial pressure at equilibrium	$\frac{(1-x)}{(1+x)} P$		$\frac{x.P}{(1+x)}$		$\frac{x.P}{(1+x)}$

Total moles at equilibrium = $(1-x) + x + x = (1+x)$.

$$K_c = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{\frac{x.P}{(1+x)} \frac{x.P}{(1+x)}}{\left[\frac{(1-x)}{(1+x)} \right]^2} = \frac{x^2 P}{(1-x)^2}$$

Substituting $x=0.82$; $P=1$ atmosphere, we get

$$K_c = \frac{(0.82)^2 \times 1}{(1+0.82)(1-0.82)} = \frac{0.82 \times 0.82}{1.82 \times 0.18} = 2.577 \text{ atmospheres.}$$

Example 7.7. Calculate the fraction of dissociation of N_2O_4 at 320 K and at a total pressure of 10 atmospheres, assuming ideal behaviour (K_p at 320 K = 0.654).

For the reaction :	$N_2O_4(g)$	\rightleftharpoons	$2NO_2(g)$
Initial	1 mole		0
At equilibrium	$(1-x)$ mole		$2x$ mole
Partial pressure	$\frac{(1-x)P}{(1+x)}$		$\frac{2xP}{(1+x)}$
Total moles = $(1-x) + 2x = (1+x)$.			

$$K_p = \frac{p_{NO_2}}{(p_{N_2O_4})} = \frac{\left[\frac{2xP}{(1+x)} \right]^2}{\frac{(1-x)P}{(1+x)}} = \frac{4x^2 \cdot P}{(1-x^2)}$$

Substituting $K_p = 0.664$; $P = 10$ atmospheres, we get

$$K_p = \frac{4x^2 \times 10}{(1-x^2)} = 0.664$$

$$40x^2 = 0.664 - 0.664x^2$$

$$\text{or } 40.664x^2 = 0.664$$

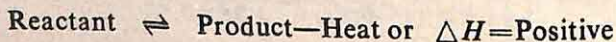
$$\text{or } x = 0.1278 \text{ or } 12.78\%.$$

7.5. LE-CHATELIER'S PRINCIPLE

A reversible reaction at equilibrium will maintain this condition indefinitely unless disturbed by changes from outside. Among such changes would be (i) the addition or removal of heat, (ii) addition or removal of a reactant or product (i.e., change of concentration), and (iii) change of pressure. The effect of changing various factors listed above to any physical or chemical equilibrium is included in a convenient and far-reaching principle termed "**Le-Chatelier's Principle**" (1884) which can be stated as follows: "*When a system in equilibrium is subjected to change in any of the factors upon which the equilibrium depends (e.g., temperature, concentration, pressure), the system will tend to adjust itself to counteract or nullify as far as possible the effect of that change.*"

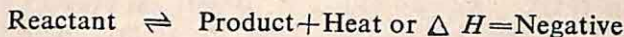
The applications of this principle, to the factors given above are discussed separately in the following paragraphs :

(1) **Influence of temperature change.** If the temperature of a system in equilibrium is increased then the equilibrium will adjust itself in the direction in which it absorbs heat. On the other hand, lowering of temperature will shift the equilibrium the direction evolving heat. Thus, if the reaction is "endothermic" i.e.,



heating the system at equilibrium causes a shift in the equilibrium

to the right with the formation of more products and hence an increase in the value of the equilibrium constant. On the other hand, if the reaction is exothermic, *i.e.*



the application of heat will cause the reaction to shift to the left, *i.e.*, more reactants will be produced at the cost of products and hence a decrease in the value of the equilibrium constant takes place. Or in the short for an *endothermic reversible reaction high temperature is favourable*; while *exothermic reactions are favoured by low temperatures*.

(2) **Influence of concentration change.** Consider a hypothetical reaction at constant temperature.



At equilibrium definite sets of concentrations of A, B, C and D will be present. Now if concentration of either of reactants A or B is increased the equilibrium will shift to the right (*i.e.*, more C and D are formed) in that way the added A or B tends to be used up. In other words, *the increase in concentration of reactants (A and B), favours the forward reaction* (see Fig. 7.3). By similar reasoning

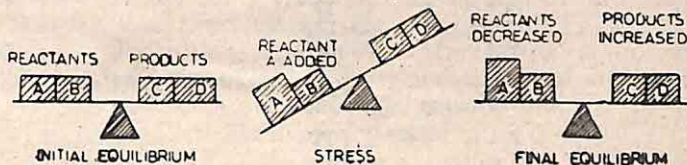


Fig. 7.3. Addition of a component causes a shift in the equilibrium of a system away from that component.

the addition of product (C or D) to the system at equilibrium causes a shift to the left with the production of more reactant (A and B).

Note. It may be added here that reactions can be made to completion by removing one of the products as it is formed. Removal of one of the products of reaction causes a negative stress, and the system tries to compensate for it in accordance with Le-Chatelier's principle by producing more of the substance being removed.

(3) **Influence of pressure change.** According to the Le-Chatelier's principle, an increase in pressure on a reversible reaction involving a gas (or gases) will try to cause the equilibrium to shift in the direction accompanied by a decrease in volume, because this would cause a decrease in pressure and hence to relieve the imposed increase. In other words, *increase of external pressure on a chemical reaction will shift the equilibrium in the direction which produces the smaller number of gaseous molecules*. On the other hand, *decreasing the pressure has the opposite effect*. If the same number of gas molecules appear on both sides of an equation (*i.e.*, when no volume change takes place), a change of pressure has no effect on the equilibrium position, because the volume of the system

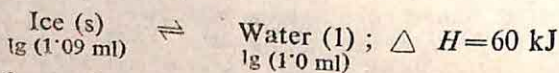
cannot decrease by having the reaction shift to either the right or left and the original equilibrium condition will persist in such a case.

The following table summarises the effect of temperature, concentration and pressure on the composition of equilibrium mixture and equilibrium constant of a reaction.

<i>Change</i>	<i>Type of reaction</i>	<i>Effect of change on the composition of equilibrium mixture</i>
(1) <i>Increase of temperature</i>	(a) Endothermic $A + B + \text{Heat} \rightleftharpoons C + D$	More, products are formed i.e., forward reaction is favoured.
	(b) Exothermic $A + B \rightleftharpoons C + D + \text{Heat}$	More reactants are formed, i.e., backward reaction is favoured.
(2) <i>Decrease of temperature</i>	(a) Endothermic	Backward reaction favoured.
	(b) Exothermic.	Forward reaction favoured.
(3) <i>Increase of pressure</i>	(a) Number of gaseous molecules decreasing $A + B \rightleftharpoons C + D$ (Larger Volume) (Smaller Volume)	Forward reaction is favoured.
	(b) Number of gaseous molecules increasing. $A + B \rightleftharpoons C + D$ (Smaller Volume) (Larger Volume)	Backward reaction is favoured.
	(c) No change in the number of gaseous molecules.	No effect.
(4) <i>Decrease of pressure.</i>	(a) Number of gaseous molecules decreasing	Backward reaction is favoured.
	(b) Number of gaseous molecules increasing.	Forward reaction is favoured.
	(c) No. change in number of gaseous molecules.	No effect.
(5) <i>Addition of reactant.</i>	$A + B \rightleftharpoons C + D$	Forward reaction is favoured.
(6) <i>Addition of product.</i>	—do—	Backward reaction is favoured.

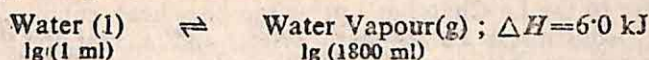
Application of Le-Chatelier's principle is illustrated below :

(1) Melting of Ice.



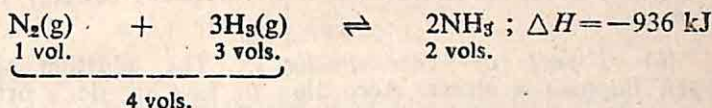
The forward reaction is accompanied by a decrease in volume and absorption of heat. Hence, both increase in pressure and temperature will favour the formation of water.

(2) Vaporization of Water.



The forward reaction is accompanied by a large increase in volume and absorption of heat. Hence, an increase in pressure will favour the backward reaction, i.e., liquefaction; while an increase of temperature will favour the forward reaction, i.e., vaporization.

(3) Formation of Ammonia (Haber's Process).



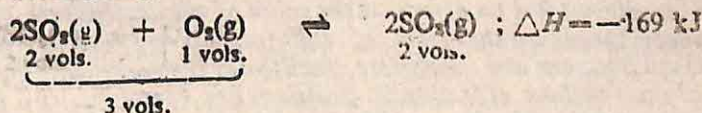
The forward reaction is exothermic and is accompanied by a decrease in volume.

(a) "Effect of temperature." If temperature is raised, the yield of NH_3 diminishes and the proportion of N_2 and H_2 in the equilibrium mixture increases. On the other hand, when the temperature is lowered, the equilibrium shifts in the direction in which heat is produced, i.e., the forward direction. Hence, low temperature favours the formation of ammonia. It may be pointed out that at low temperature, the equilibrium is reached very slowly. Even with catalyst, the rate of reaction is not rapid at low temperature. Hence, a compromise is to be made between low temperature and time required for equilibrium to be reached. A temperature of 775K is generally used.

(b) "Effect of pressure". If at a constant temperature, pressure is increased, the reaction will proceed in the direction accompanied by a decrease in volume, i.e., the forward reaction. Hence high pressure favours the formation of ammonia.

(c) "Effect of increasing concentration of reactants". By increase in the quantity of one or both on the reactant (N_2 or H_2) to the equilibrium mixture, the reaction will proceed in the direction in which the added components are used up, i.e., the forward direction. Hence high concentration of N_2 or H_2 (or both) favour the formation of NH_3 .

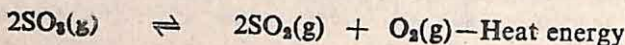
(4) Oxidation of SO_2 to SO_3 (Contact Process for the manufacture of H_2SO_4).



The forward reaction is exothermic and is accompanied by a decrease in volume.

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(a) "Effect of temperature". If temperature is raised, then according to the Le-Chatelier's principle the heat supplied to the mixture, constitutes an imposed stress and a reaction will take place to counter this stress, i.e., the resulting reaction is such that it tends to lower the temperature. But a reaction that lowers temperature is endothermic and it is the reverse of the exothermic reaction, i.e.,

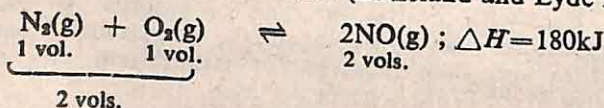


In other words, as the temperature rises, the yield of $\text{SO}_3(\text{g})$ diminishes and the concentration of the reactants, $(\text{SO}_2(\text{g}) + \text{O}_2(\text{g}))$ increases.

(b) "Effect of concentration". The addition of more oxygen imposes a stress. According to Le-Chatelier's principle, to counteract this stress, more $\text{SO}_3(\text{g})$ will be formed thereby decreasing the concentration of $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$.

(c) "Effect of pressure." The forward reaction is attended by a decrease in volume. If this reaction takes place in a closed container, it is apparent that forward reaction is attended by decrease in gas pressure. On the other hand, if the reaction proceeds to the left, the pressure is increased. By Le-Chatelier's principle, if pressure on the gas is increased, the yield of $\text{SO}_3(\text{g})$ would increase.

(5) Formation of Nitric Oxide (Birkeland and Eyde Process).



The forward reaction is endothermic and no change in volume occurs.

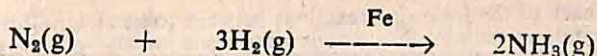
(a) "Effect of temperature". As the forward reaction is accompanied by an absorption of heat, consequently an increase of temperature will favour formation of $\text{NO}(\text{g})$.

(b) "Effect of pressure." As the forward reaction is accompanied by no change in volume, consequently the pressure will have no effect on the equilibrium.

(c) "Effect of concentration". The formation of $\text{NO}_2(\text{g})$ will be favoured by an excess of $\text{O}_2(\text{g})$ or $\text{N}_2(\text{g})$ or both.

7.6. EFFECT OF CATALYST ON THE EQUILIBRIUM

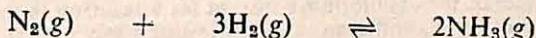
A catalyst has no effect on the value of the equilibrium constant. It merely speeds up the rates of the forward and reverse reactions to an equal extent and, therefore, facilitates the early attainment of equilibrium without affecting its position. For example, iron powder is used as catalyst in the production of ammonia from nitrogen and hydrogen to increase the rate of reaction of these two elements.



However, the same catalyst serves equally well to increase the rate of the reverse reaction, *i.e.*, the decomposition of ammonia into its constituent element.



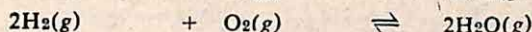
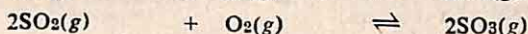
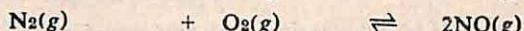
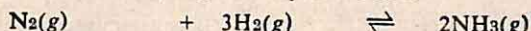
Thus, the net effect of iron on the reversible reaction is to cause equilibrium to be reached more rapidly.



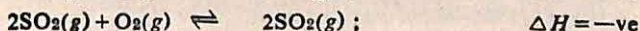
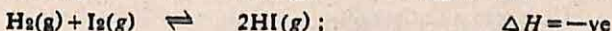
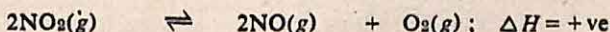
QUESTIONS

(A) Essay Type

1. Characterize a reversible reaction and give an example of one.
2. List the factors that determine the rate of a reaction.
3. Explain the terms chemical equilibrium and equilibrium constant. Using the law of mass action, derive the mathematical expression of the chemical equilibrium for the following reversible reactions.

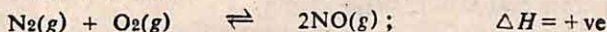
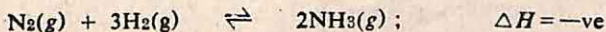


4. How is the speed of reaction $\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$ affected by doubling the initial concentrations of A and B?
5. State Le-Chatelier's principle. State the conditions which favour the forward reactions in the following equilibria and explain why.



6. Under what conditions do changes in pressure affect the system in equilibrium?

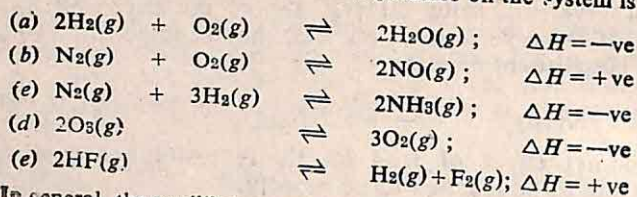
7. How will an increase in temperature affect the following equilibria?



8. What is the effect of a catalyst upon the equilibrium constant of a system? Of what value is a catalyst for a system that attains equilibrium?

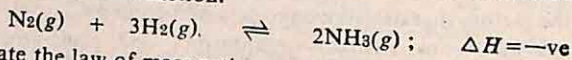
9. In the reaction between hydrogen and sulphur to produce H_2S , energy is liberated as H_2S is made. How should the pressure and temperature be adjusted in order to improve the equilibrium yield of H_2S , assuming conditions such that all reactants and products are in the gaseous state.

10. For each of the following reactions between gases at equilibrium, determine the effect upon the equilibrium concentrations of the products when the temperature is decreased; when the external pressure on the system is decreased.

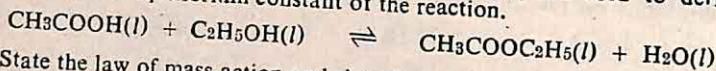


11. In general, the equilibrium constant for a reaction in the gaseous phase has different units and a different numerical value when partial pressures rather than concentration's are used in the equilibrium constant expression. Show that such is not the case when the decomposition of HI to H_2 and I_2 ; show that the numerical value of the equilibrium constant would be independent of the units in which concentration is expressed for this particular reaction.

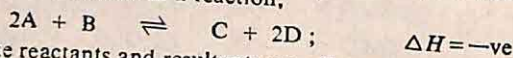
12. Suggest three ways in which the equilibrium concentration of ammonia can be increased for the reaction.



13. State the law of mass action, and show how it may be used to derive an expression for the equilibrium constant of the reaction.



14. State the law of mass action and show how you would use it to derive the equilibrium constant of a reaction,



in which the reactants and resultants are all gases.

What steps could be taken (a) to obtain a large as possible of C from a given amount of B, and (b) to obtain the yield as quickly as possible?

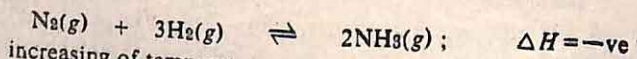
(B) Objective type

15. Point out the correct statement in each of the following :

- (a) In the reaction: $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$; the forward reaction is favoured by
 (i) increase of pressure,
 (ii) decrease of pressure,
 (iii) keeping the pressure constant.

- (b) Law of mass action states that the rate of a chemical reaction is directly proportional to one of the following
 (i) volume of the container,
 (ii) equilibrium constant,
 (iii) nature of reactant,
 (iv) molar concentrations of the reactants.

(c) In the reaction :



increasing of temperature

- (i) shifts the equilibrium to the right,
 (ii) shifts the equilibrium to the left,
 (iii) does not alter the equilibrium.

16. For the reaction : $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$; $K=50$. At equilibrium
- forward reaction is predominant.
 - backward reaction is predominant.
 - both forward and back ward reaction take place at the same rate.
 - none of the reactions take place.
17. In a chemical reaction, equilibrium has been established when
- opposing reactions cease.
 - concentrations of reactants and products are equal.
 - velocity of the reverse process is equal to that of the forward process.
 - no heat is lost or gained by the system.
 - all reactants have reacted.
18. In the reaction :

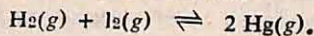


the equilibrium is shifted to the left on

- decreasing the pressure and increasing the temperature.
 - decreasing the pressure and decreasing the temperature.
 - increasing the pressure and increasing the temperature.
 - increasing the pressure and decreasing the temperature.
 - adding more A_2 gas.
19. What are the conditions which favour the forward reaction in the following equilibrium ?
- $$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}); \quad \Delta H = -ve$$
- high temperature, high pressure.
 - low temperature, high pressure.
 - use of a catalyst.
 - none of these.
20. Complete the followings :
- According to the law of mass action, the rate at which a substance is reacting is.....molar concentration.
 - At equilibrium the rate of forward reaction.....the rate of backward reaction.
 - According to Le-Chatelier's principle high pressure favours the reactions accompanied by.....volume.

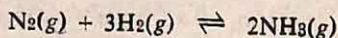
C) Numerical Problems

21. 0.25 mole of H_2 and 0.18 mole of I_2 vapours were sealed in a glass bulb at 725 K. At the equilibrium 0.308 moles of HI was formed. Calculate the equilibrium constant for the reaction,



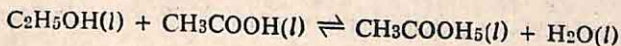
(Ans. 38.0)

22. Nitrogen reacts with hydrogen to give ammonia according to the equation,



An equilibrium mixture of the above at 673 K was found to contain 0.6 mole of nitrogen, 0.4 mole of hydrogen, and 0.14 mole of ammonia in a litre. Calculate the equilibrium constant for the system. (Ans. 0.51 litre² mole⁻²)

23. Ethanol and acetic acid interact to form ethyl acetate and water, according to the equation,



When one mole each of the alcohol and the acid are allowed to react at 373K in a sealed tube, equilibrium is established when one-third of a mole of each of the reactants remains. Calculate equilibrium constant. (Ans. 4.0)

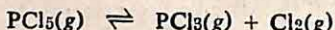
24. Two moles of PCl_5 are placed in a 5 litre container. Dissociation takes place according to the equation,



At equilibrium, 0.4 mole of Cl_2 is present. Calculate the value of the equilibrium constant for this reaction under the conditions of the experiment.

(Ans. 0.02 mole litre⁻¹)

25. Write the mathematical expression of the law of chemical equilibrium for the reversible reaction.



At one atmosphere and 523 K, PCl_5 is 80% dissociated, calculate the equilibrium constant.

(Ans. 1.778 atm.)



Electrolytic Dissociation and Ionic Equilibrium

8.1. ELECTROLYTIC CONDUCTION

Substances differ enormously in the resistance which they offer to the passage of electricity. Thus, if the same voltage is applied to a bar of copper and a bar of sulphur of the same dimensions, the current flowing through the copper is many million million times as great which flows through the sulphur. *A substance, like copper, which allows electricity to pass through it is called a conductor; while a substance, such as sulphur, which does not allow electricity to pass through it is called a non-conductor.* Other members of this class are organic substances like alcohol, urea, sugar, etc., in their solid as well as in the liquid state. When a current is passed through a copper wire, the wire is heated by the passage of the current, but is otherwise unchanged; and when the current is cut off, it regains its original properties as soon as it has cooled down to its original temperature. When, an electric current is passed through dilute sulphuric acid, the passage of electricity through the solution is accompanied by a chemical decomposition, since hydrogen is given off at one electrode and oxygen at the other, and this decomposition continues as long as the current flows.

Substances which conduct electricity without suffering any permanent change are termed "metallic conductors". All metals belong to this class and also a few non-metallic substances, like gas carbon, arsenic, selenium, which all have small metallic conductivity. *In metallic conduction an electric current consists of a movement of electrons only and it, obviously, does not involve any chemical change in the metal.*

Substances which conduct electricity, and simultaneously undergo a chemical change were described by Faraday as electrolytes, (i.e., decomposed by electricity). To this class belongs fused

salts, aqueous and alcoholic solutions of salts, acids and bases. Pure water is such a feeble electrolyte that it is often classed as non-conductor, *In electrolytic conduction the current is carried by charged particles of electrolyte, called ions.*

The conduction of electricity by an electrolyte, differs from metallic conduction in two main aspects. Firstly, electrolytic conduction is invariably accompanied by chemical changes; whereas only physical changes occur when an electric current passes through a piece of metal. The second difference concerns in the way in which conductivity varies with temperature. An electrolytic conductor conducts electricity more readily at higher temperature; whereas in metals the reverse is the case.

8.2. ELECTROLYSIS

Electrolysis is the phenomenon in which electric energy is used to change the chemical identity of electrolytes. Actually an electrolysis involves two distinct physical processes and each causes a chemical transformation. The two physical processes occur at two different electrodes which are immersed in or are in contact with the liquid medium containing an electrolyte. By means of a battery or a source of direct current, electricity (electrons) is 'pumped' from one electrode, the *anode*, to the other, the *cathode*. In the liquid medium, the mobile positive ions (called *cations*) are attracted to the cathode, and the mobile negative ions (called *anions*) to the anode. At the anode, the negative ions transfer (donate) electrons to the anode. At the cathode the positive ions receive (accept) electrons from the cathode. Because of migration of the ions, the liquid appears to conduct an electric current. The current is said to flow, conventionally, from the positive to the negative electrode outside the electrolytic solution. The anions on giving up their electrons to the anode become zero charged and are subsequently

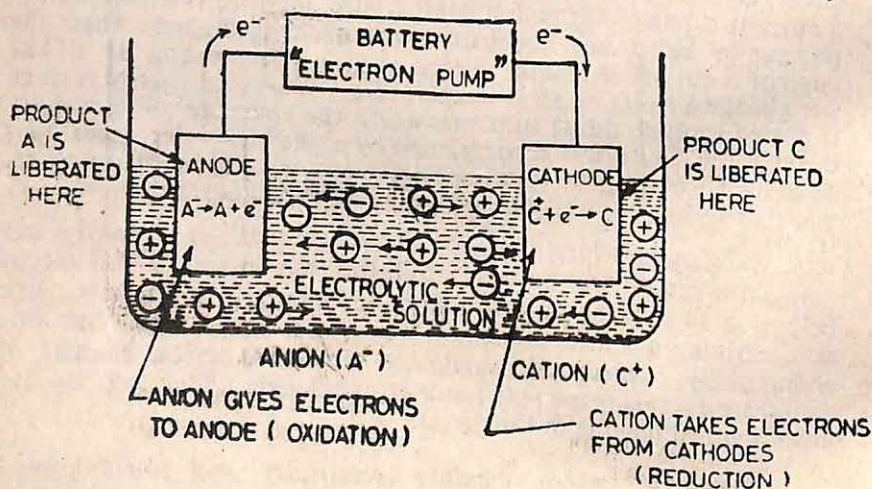
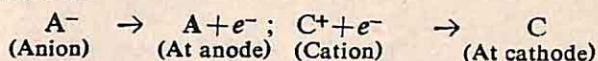


Fig. 8.1. The process of a simple electrolysis.

discharged ; while the cations are discharged at the cathode after taking electrons.



Thus, A and C will be the products of electrolysis, A being liberated to the anode and C at the cathode.

The giving up of the electrons to the anode and the taking of electrons from the cathode maintains the flow of current. The whole process of a simple electrolysis is illustrated in diagrammatic form, in Fig. 8.1. Consequently, the electrode process taking place at the anode (a giving of electrons) is an oxidation process ; and that at the cathode (a taking of electrons) is reduction process.

8.3. LAWS OF ELECTROLYSIS

In 1833 Michael Faraday, a British scientist, summarised his experimental results in his **laws of electrolysis**.

(1) *The products of electrolysis appear only at the electrodes, i.e., at the point at which the current enters and leaves the solution.*

(2) *The amount (m) of substance decomposed in electrolysis is proportional to the quantity of electricity which passes through the electrolyte.* This law, which is generally known as **Faraday's first law of electrolysis**, implies that the amount of decomposition is independent of the temperature of the solution, of the current density and of the material of electrodes and vessel.

Now the quantity of electricity (in coulombs) is given by the steady current, I (in amperes) multiplied by the time, t (in seconds).

$$\begin{array}{l} \therefore m \propto It \\ \text{or} \quad m = Z It \end{array}$$

where Z is a constant known as the *electrochemical equivalent* of the substance. Thus, if $I=1$ ampere, $t=1$ sec. ; $m=Z$. So, *electrochemical equivalent of a substance is the mass in gram set free by the passage of 1 coulomb, (e.g., 1 ampere for 1 second) of electricity, e.g.,*

$$Z \text{ for silver} = 1.116 \times 10^{-3}$$

$$Z \text{ for copper} = 3.2935 \times 10^{-4}$$

$$Z \text{ for hydrogen} = 1.0446 \times 10^{-5}$$

(3) *The masses of different products set free by passing same quantity of electricity through a series of solutions of different electrolytes are proportional to their chemical equivalents.*

$$\text{i.e., } \frac{m_1}{m_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}$$

where m_1 and m_2 are the masses liberated by the same quantity of

electricity ($=I \times t$) from substances with chemical equivalents E_1

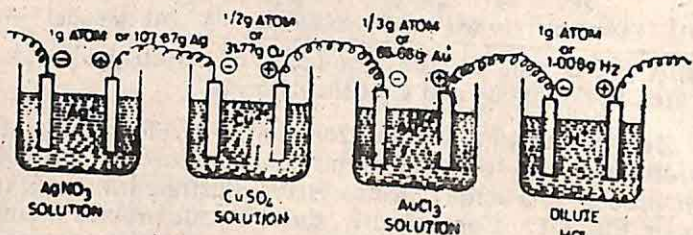


Fig. 8.2. Electrolysis in series. Amounts of various metals discharged by 1 Faraday (96,500 Coulombs) of electricity.

and E , respectively. It follows from this law (called, second law of electrolysis) that E/Z is a constant. The quantity of electricity which liberates 1 gram equivalent of any substance is termed a Faraday (F) and is equal to 96,500 coulombs. Thus,

$$F = 96,500 = \frac{\text{Chemical equivalent (E)}}{\text{Electrochemical equivalent (Z)}}$$

But from first law, $Z = m/It$

$$\therefore m = \frac{I \times t \times \text{Chemical equivalent}}{96,500}$$

Consequently, this law can be used to determine the chemical equivalent.

Example 8.1. Calculate the amount of copper deposited by the passage 1.5 amperes electric current for an hour through copper sulphate solution (electrochemical equivalent of copper is 0.00033).

Here $Z = 0.00033$; $I = 3.5$ amp.; $t = 1$ hour = 3600 sec.

$$\therefore m = Z It = 0.00033 \text{ g} \times 1.5 \times 3,600 = 1.782 \text{ g of copper.}$$

Example 8.2. Calculate the mass of copper deposited on the cathode when a current of 0.2 ampere is passed through a solution of copper sulphate for 10 minutes. The chemical equivalent of copper is 31.78.

Here $E = 31.78$; $I = 0.2$ amp.; $t = 10$ min. = 600 sec.

$$\therefore m = \frac{I t E}{96,500} = \frac{0.2 \times 600 \times 31.78}{96,500} \text{ g.} = 0.0395 \text{ g of copper.}$$

Example 8.3. What current strength in amperes will be required to liberate 10g of iodine from KI solution in 1 hour? (Chemical equivalent of iodine = 127)

Here $E=127$; $m=10$ g ; $t=1$ hour $=36,00$ sec. ; $I=?$

$$\begin{aligned}\text{But } m &= \frac{I t E}{96,500} \\ \therefore I &= \frac{m \times 96,500}{t \times E} \\ &= \frac{10 \times 96,500}{3600 \times 127} \text{ amp.} \\ &= 2.11 \text{ amp.}\end{aligned}$$

Example 8.4. A current of 0.2 ampere is passed through a solution of cupric sulphate for 10 minutes, using platinum electrodes. Calculate the number of atoms of copper deposited on the cathode.

$$\begin{aligned}\text{Amount of electricity passed} &= I \times t \\ &= 0.2 \text{ amp.} \times 600 \text{ sec.} \\ &= 120 \text{ coulombs.}\end{aligned}$$

$$\begin{aligned}\text{But } 96,500 \text{ coulombs} &= 1 \text{ g equivalent of copper,} \\ &= \frac{1}{2} \text{ g atom of copper.} \\ \therefore \text{Chemical equivalent of copper} &= \frac{1}{2} \times \text{atomic mass.} \\ &= \frac{1}{2} \times 6.023 \times 10^{23} \text{ atoms of copper.}\end{aligned}$$

$$\begin{aligned}\therefore 120 \text{ coulombs} &= \frac{\frac{1}{2} \times 6.022 \times 10^{23} \times 120}{96,500} \text{ atoms of copper.} \\ &= 3.875 \times 10^{19} \text{ atoms of copper.}\end{aligned}$$

Example 8.5. What mass of silver is deposited from a solution of silver nitrate by a current of 0.075 ampere flowing for 17 minutes ? The electrochemical equivalent of silver is 1.118×10^{-3} . Given also that chemical equivalents of copper and silver are 31.75 and 107.9 respectively. what mass of copper is deposited by the passage of the same quantity of electricity.

$$\begin{aligned}\text{Mass of silver deposited, } m &= ZIt \\ &= 1.113 \times 10^{-3} \times 0.075 \times 17 \times 60 \text{ g} \\ &= 0.0856 \text{ g.}\end{aligned}$$

$$\text{Now } \frac{m_1}{E_1} = \frac{m_2}{E_2} \quad (\text{From Faraday's 2nd law})$$

Here if $m_1=0.0856$ g (for silver) ; $E_1=107.9$; $E_2=31.75$ (for copper). Therefore, mass of copper deposited,

$$\begin{aligned}m_2 &= \frac{m_1 E_2}{E_1} \\ &= \frac{0.0856 \times 31.75}{107.9} \text{ g} \\ &= 0.0252 \text{ g.}\end{aligned}$$

Example 8.6. A current of 0.5 ampere is passed through an acidified solution for 1 hour. What volume of hydrogen will be liberated at STP? (Chemical equivalent of hydrogen = 1).

Here $E=1$; $I=0.5$ amp ; $t=1$ hour $=3600$ sec.

$$\therefore m = \frac{I t E}{96,500} = \frac{0.5 \times 3600 \times 1}{96,500} \text{ g} = \frac{18}{965} \text{ g}.$$

But 2g of H_2 at STP occupies = 22,400 ml.

$$\therefore \frac{18}{965} \text{ g } \text{,,} \quad \text{,,} \quad \text{,,} \quad = \frac{22,400 \times 18}{2 \times 965} \text{ ml.}$$

$$= 208.7 \text{ ml.}$$

8.4. INDUSTRIAL APPLICATIONS OF ELECTROLYSIS

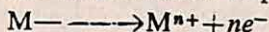
1. Electrolytic preparations. Electrolysis is widely used as a means of producing elemental substances by oxidation or reduction. Thus, aluminium, sodium, potassium, magnesium, calcium are produced exclusively by electrolysis. Chlorine is produced almost entirely by the electrolysis of sodium chloride. Practically all of the sodium hydroxide (caustic soda) is produced commercially as a by-product of the electrolysis of a aqueous sodium chloride. All elemental fluorine is also made by electrolysis. Some examples of electrolysis preparations are tabulated very briefly in Table 8.1. The example also illustrate the fact that, although oxidation and reduction always occur simultaneously, they can be separated in certain ionic systems.

Table 8.1. *Typical industrial electrolysis.*

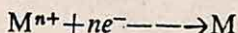
<i>Principal electrolyte</i>	<i>Reaction at the anode (oxidation)</i>	<i>Reaction at the cathode (reduction)</i>
1. Molten mixture of Al_2O_3 (from bauxite) and Na_3AlF_6 (cryolite)	$\text{O}^{2-} \rightarrow \text{O} + 2e^-$;	$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$
2. Molten $\text{Mg}^{2+} (\text{Cl}^-)_2$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$;	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$
3. Molten $\text{Na}^+ \text{Cl}^-$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$;	$\text{Na}^+ + e^- \rightarrow \text{Na} + \text{H}_2\text{O}$ $\text{NaOH} + \frac{1}{2}\text{H}_2$
4. Molten $\text{Li}^+ \text{Br}^-$	$2\text{Br}^- \rightarrow \text{Br}_2 + 2e^-$;	$\text{Li}^+ + e^- \rightarrow \text{Li}$
5. Molten $\text{Ca}^{2+} (\text{Cl}^-)_2$	$2\text{Cl}^- \rightarrow \text{Cl}_2 + 2e^-$;	$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$
6. Molten mixture of $\text{K}^+ \text{F}^-$ and HF	$2\text{F}^- \rightarrow \text{F}_2 + 2e^-$;	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$
7. Water plus a trace of H_2SO_4	$2\text{H}_2\text{O} \rightarrow \text{O} + 4e^-$;	$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$

2. **Electrolytic refining of metals.** Certain metals must be produced in a very pure state, if they are to be used for specific purposes. For example, the electronic conductance of copper is appreciably retarded by the presence of even traces of other elements. Production of metals in a high state of purity is called *electrolytic refining* or *electro-refining*. The process consists in essence, of

controlled electrolysis. In the electrolytic cell, the anode is a block of impure metal and the cathode is a thin sheet of the pure metal. The electrolyte, in the cell liquid, contains some ionic compound of the metal. During the operation of the cell, metal leaves the anode because it is oxidised to positive ions.



The positive ions formed at the anode migrate towards the cathode where they are reduced.



By careful control of the voltage of the cell, only the atom of the metal being refined are deposited on the pure cathode. The impurities either remain in solution or produce an undissolved 'mud' near the anode. Electrolytic refining is used for refining of gold, silver, copper (see Fig. 8.3) and zinc.

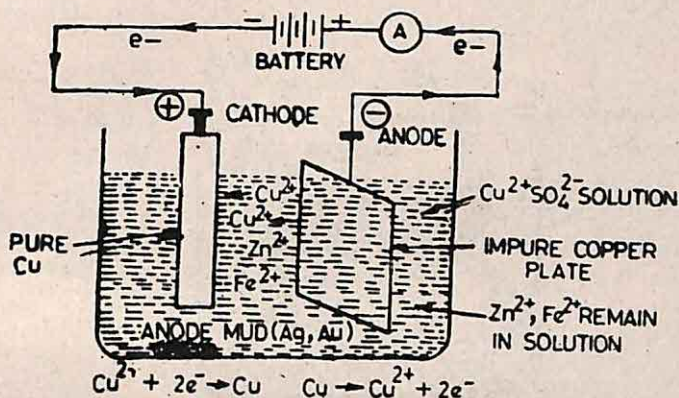


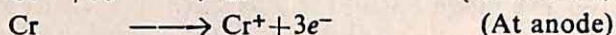
Fig. 8.3. Electrolytic refining of copper.

3. **Electroplating or electrodeposition** is a process in which a thin film or deposit of a superior metal like gold, silver, nickel, chromium is produced electrolytically on the surface of a base metal (like copper, iron, etc.). Electroplating is carried out with the following objects :

- (i) '*Decoration*' e.g., to enhance the beauty of copper, silver or gold is deposited over it.
- (ii) '*Preservation*' e.g., metals like iron are electroplated with nickel or chromium to protect them from rusting.
- (iii) '*Repairs*' e.g., broken parts of machinery may be repaired by electrodeposition of metal.

In electroplating the article to be plated is made the cathode and suspended in a bath containing a soluble salt of the metal to be deposited. The anode is made of the metal to be deposited. On the passage of the electric current, metal ions from the electrolyte

are deposited on the article at the cathode and an equivalent amount of metal dissolves from anode into the electrolytic solution. For example, in the electroplating of chromium.



The properties of the electroplated coating, depend on the composition of the electrolytic solution, current density, temperature of the electrolytic bath and acidity of bath. For finer, smoother and brighter deposit ion low temperature, high current density and high metal ion concentration in the bath are employed.

In electroplating of silver, the electrolyte is normally an argentocyanide *e.g.*, $\text{KAg}(\text{CN})_2$ instead of simple salt (like AgNO_3) because of this silver sticks more firmly to the article when deposited

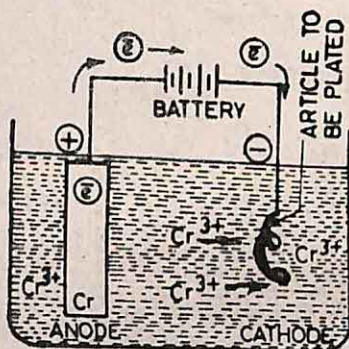
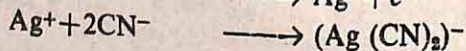
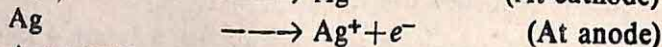
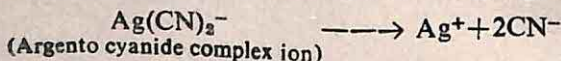


Fig. 8.4 Electroplating of chromium.

from, $\text{Ag}(\text{CN})_2$ ions. The complex ions are in equilibrium with Ag^+ and CN^- ions in solution and when some of the Ag^+ ions have been deposited more are formed by dissolving Ag anode.



4. **Electrotyping** involves the deposition of a thin layer of a metal on a cut out pattern created with graphite to make it conducting. The pattern is made the cathode in the cell and a block of the metal forms the anode. After the typing has been completed, the metal foil is removed from the pattern and backed by a strip of another metal to strengthen it.

8.5. CONDUCTIVITY OF ELECTROLYTES

The resistance of a conductor such as silver is directly proportional to its length and inversely proportional to its cross-sectional area (Ohm's Law).

i.e., $R = \rho \frac{l}{A}$ where R = Resistance in ohms.

ρ = specific resistance or resistivity.

l = length in cm.

A = area of cross-section in cm^2 .

Thus, if $l = 1 \text{ cm.}$; $A = 1 \text{ cm}^2$; $R = \rho$, i.e., specific resistance of a conductor, which is a constant for any given substance, is the resistance between two opposite faces of a centimeter cube of that substance.

The reciprocal of the specific resistance is called the *specific conductivity* (κ), i.e.,

$$\kappa = \frac{1}{\rho} = \frac{l}{AR} \text{ ohm}^{-1} \text{ cm}^{-1}$$

The reciprocal of the resistance is termed as the conductance.

i.e., conductance $= 1/R = kA/l \text{ ohm}^{-1}$

Thus, if $l = 1 \text{ cm.}$; $A = 1 \text{ cm}^2$; $k = 1/R$ = conductance. Hence, **specific conductivity (κ) is the conductance of a one centimeter cube of the substance or solution.** The unit of specific conductance is $\text{ohm}^{-1} \text{ cm}^{-1}$ or mhos cm^{-1} ,

since,

$$\kappa = \frac{1}{\rho} = \frac{l}{RA} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \text{ohm}^{-1} \text{ cm}^{-1}.$$

The greater the specific conductance, the more readily does the electrolyte allow the passage of an electric current through it.

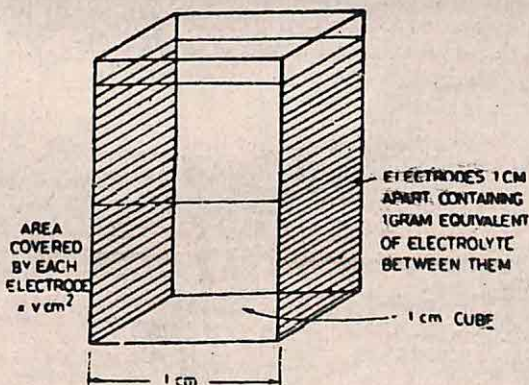


Fig. 8.5.

The specific conductance of an electrolyte depends not only upon its nature but also upon the concentration of the solution.

For electrolytes, it is convenient to define a term called the **equivalent conductivity**, represented by the symbol, λ_v . It represents the conductance of all the ions present in 1 gram equivalent of the electrolyte in the solution. Consider two large electrodes (Fig. 8.5) 1 cm apart, and let the whole of the solution ('v' ml) containing 1 gram equivalent be placed between the electrodes. The area covered on each electrode is $v \text{ cm}^2$. But conductance of 1 cm^3 of solution is specific conductance.

$$\therefore \lambda_v = v \times \text{specific conductance of } 1 \text{ cm}^3 \text{ solution.} \quad \dots (i)$$

$$= v \times \kappa$$

If c is the concentration in gram equivalents per litre then,

$$= \frac{1000 \kappa}{c} \quad \dots (ii)$$

The **molecular conductivity** (μ_v) is defined, in the similar way, as the conductance of all the ions present in one mole of electrolyte in the solution. If M is the molar concentration, then

$$\mu_v = \frac{1000 \kappa}{M} \quad \dots (iii)$$

Measurement of conductance. This is normally carried out by the use of Wheatstone bridge. However, the measurement of the conductivity of an electrolyte is complicated by the fact that if a direct current is used with the usual "Wheatstone bridge" apparatus, the products of electrolysis collect at the electrodes and set up a *back emf*, i.e., back potential which apparently increase the resistance of the electrolyte. This difficulty is overcome by using an alternating current from an induction coil with a frequency of 1000 cycles per second (i.e., the directions of the current is reversed 1000 times in a second), and detecting the flow of current with a 'head telephone' in place of galvanometer. The arrangement of the apparatus is shown in Fig. 8.6.

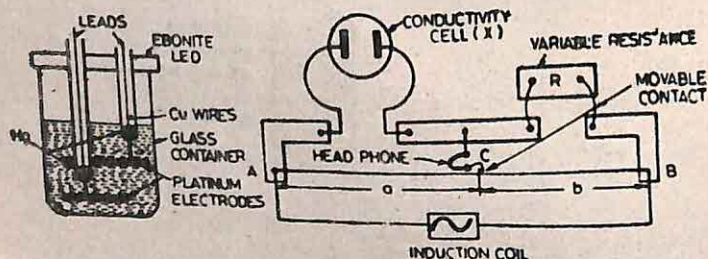


Fig. 8.6. (a) Conductivity cell, (b) Measurement of conduction.

Solution under examination is filled in a conductivity cell (see Fig. 8.6a). It is made of specially resistant glass and is fitted

with two platinum electrodes (usually coated with platinum black) which are fixed rigidly in position so that their distance apart is constant. The cell is made one arm of the bridge. When the apparatus is connected up in this manner, a sound will be heard in the telephone but in one position of the moveable contact C the sound will be reduced to a minimum. This gives the null point (or balance point). When this adjustment has been made, then

$$\frac{\text{Resistance (X)}}{\text{Resistance (R)}} = \frac{a}{b}$$

$$\text{i.e., Resistance of cell (X)} = \frac{a}{b} \times R$$

where R is the known resistance corresponding with the plugs which have been removed from the resistance box; while 'a' and 'b' are the length of wire between the moveable contact and the ends of the bridge wire.

Now in order to calculate the specific conductivity of an electrolyte the observed resistance (X) of the cell which contains it, the dimension l and A of latter must be known. Since the electrodes of an ordinary cell are always slightly irregular, its dimensions can not be determined by direct measurement. However, measurement of cell dimensions are made indirectly. The cell used is standardized by means of an electrolyte of known resistance (e.g., $\text{N}/50\text{K}+\text{Cl}^-$) which has been determined previously in a cell of accurately known dimensions. As l and A are constant for a given cell, so is the ratio l/A . This is called the cell constant (C)

$$\text{i.e., } \kappa = (1/R) \times (l/A) = (1/R) \times (C)$$

$$\text{or } C = \kappa R = l/A$$

.....(iv)

Thus, unit of cell constant is cm^{-1} . Therefore, cell constant (C) is the factor which must be multiplied to observed conductivity ($1/R$) to get the specific conductivity.

The specific conductivity κ , of the electrolyte is then calculated from the equation (iv). If the concentration of solution is known (in gram equivalent per litre), the equivalent conductance (λ_e) can also be calculated employing the formula (ii).

Example 8.7. The resistance of a conductivity cell containing 0.2 N nickel sulphate solution at 298 K is 104.3 ohms; while the resistance of the cell containing 0.02 N KCl solution is 550 ohm at 298 K. If the specific conductivity of 0.02 N KCl solution is $0.00277 \text{ mhos cm}^{-1}$ at 298 K, find the specific and equivalent conductivities of the nickel sulphate solution.

$$\begin{aligned} \text{Cell constant (C)} &= \text{Sp. cond.} \times \text{Resistance of } 0.02 \times \text{KCl} \\ &= 0.00277 \times 550 \text{ cm}^{-1} \\ &= 1.5235 \text{ cm}^{-1}. \end{aligned}$$

$$\begin{aligned} \text{Sp. conductivity of nickel sulphate solution, } \kappa \\ &= \frac{\text{cell constant}}{\text{Resistance}} \end{aligned}$$

$$= \frac{1.5235 \text{ cm}^{-1}}{104.3 \text{ ohm}} = 0.0146 \text{ mho cm}^{-1}.$$

Since the nickal sulphate solution is 0.2 N it contains 0.2 gram equivalent per litre. So, concentration,

$$c = 0.2 \text{ gram equivalent/litre.}$$

∴ Equivalent conductivity of solution

$$\begin{aligned} \lambda_v &= \frac{1000\kappa}{c} \\ &= \frac{1000 \times 0.0146}{0.2} \\ &= 73.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ at } 298 \text{ K} \end{aligned}$$

8.6. VARIATION OF CONDUCTIVITY WITH DILUTION

The conducting power of an electrolyte is due to ions and this increases with increasing dilution, since the degree of dissociation of electrolyte increases with dilution. In other words, the equivalent (or molecular) conductivity increases as the number of ions present in a solution containing 1 gram equivalent (or gram molecule) of electrolyte increases with dilution. However, there are two general ways in which equivalent conductivity varies with concentrations as shown in Fig. 8.7, where equivalent conductivity is plotted against the dilution (i.e., the volume of solution containing a gram-equivalent of electrolyte). Curve 'A' is typical of most salts, and of

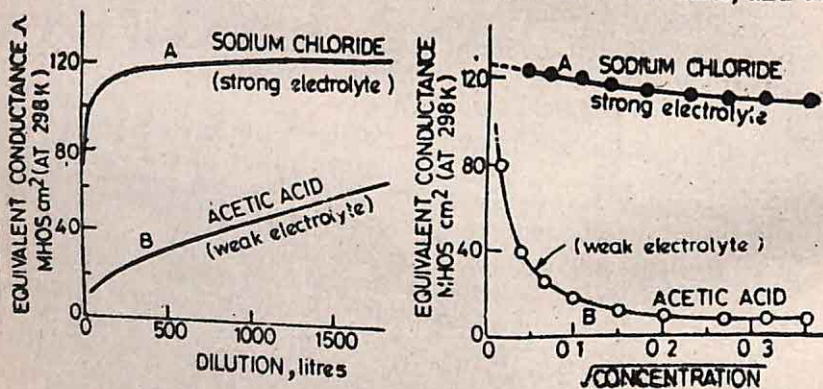


Fig 8.6. (a) Variation of equivalent conductance with dilution, (b) Variation of equivalent conductance with square root of concentration.

hydrochloric, sulphuric, and nitric acids, and also of sodium and potassium hydroxides. In these cases the conductance is always high and increases only slightly with dilution, soon, reaching a maximum value known as the **equivalent conductance at infinite dilution** (i.e., solution is so dilute that further dilution does not change the value of λ_v) and denoted by λ_∞ . Substances whose equivalent conductances varies in this way are known as "strong

electrolytes" On the other hand, curve 'B' is typical of most organic acids (oxalic, acetic, etc.) and amines and of ammonium hydroxide, and of certain mercury salts. In concentrated solution the equivalent conductivity is very low but it increases steadily with dilution. Substances of this type are known as '**weak electrolytes**'. However, no sharp distinction exists between the two types of electrolytes, since electrolytes of intermediate behaviour exists, particularly the salts of transitional metals of dibasic acids (e.g., NiSO_4 , MnSO_4).

The equivalent conductivity of strong electrolytes at infinite dilution is best determined by plotting their equivalent conductance against the square root of their concentration, c , in gram equivalent per litre, and extrapolating the graph at $c=0$, since c is zero at infinite dilution. This is illustrated in Fig. 8.7 (b), where the values for sodium chloride have been plotted. It will be noticed that there is a linear relationship between λ_0 and c when concentration is small. The graphs of other strong electrolytes are similar.

Weak electrolytes also have a characteristic value for the equivalent conductance to infinite dilution, but in their case it cannot be determined directly, as Fig. 8.7 (b) shows, the graph is not a straight line.

Specific conductivity (κ) depends (a) upon the number of ions, and (b) on the amount of water present. Consequently, as the dilution increases (i.e., amount of water increases) the conducting power of 1 cm cube of the electrolyte decreases, owing to the fact there are less ions and more water molecules present in 1 cm cube.

8.7. KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS

In 1876, Kohlrausch noticed that pairs of sodium and potassium salts with the same anion showed a constant difference in equivalent conductance to infinite dilution (see Table 8.2). Kohlrausch concluded that "*at infinite dilution each ion shows a characteristic conductance which is independent of the other ions*

Table 8.2. *Equivalent Conductance at Infinite Dilution.*

Salt	At 291K	
K^+Cl^-	130.1	Mhos cm^2
Na^+Cl^-	109.1	"
K^+NO_3^-	126.3	"
Na^+NO_3^-	105.3	"

} Difference = 21.1 mhos cm^2

} Difference = 21.1 mhos cm^2

present in the solution". Thus, equivalent conductivity of any electrolyte is equal to the sum of the equivalent conductance of

its cation and anion, since each ion contributes a definite amount to the total conductance of the electrolyte,

$$\text{i.e., } \lambda_{\infty} = \lambda_{+} + \lambda_{-}$$

where λ_{+} and λ_{-} are the ionic conductance at infinite dilution of cation and anion respectively.

The importance of this law is that it can be used to calculate the equivalent conductances at infinite dilution of weak electrolytes which cannot be determined by extrapolation as already discussed in section 8.6. The calculation is illustrated by the following example.

Example 8.8. Calculate the equivalent conductivity at infinite dilution of acetic acid at 298K, given that at that temperature the equivalent conductivities at infinite dilution of hydrochloric acid, sodium chloride, and sodium acetate are 426, 126 and 91 mhos cm^2 respectively.

$$\begin{aligned} \text{(i)} \quad & (\text{H}^{+}\text{Cl}^{-}) = (\text{H}^{+}) + (\text{Cl}^{-}) = 426 \text{ mhos cm}^2 \\ \text{(ii)} \quad & (\text{Na}^{+}\text{Cl}^{-}) = (\text{Na}^{+}) + (\text{Cl}^{-}) = 126 \text{ mhos cm}^2 \\ \text{(iii)} \quad & (\text{Na}^{+}\text{Ac}^{-}) = (\text{Na}^{+}) + (\text{Ac}^{-}) = 91 \text{ mhos cm}^2 \\ \therefore \quad & (\text{H}^{+}\text{Ac}^{-}) = (\text{H}^{+}) + (\text{Ac}^{-}) = \text{(i)} + \text{(iii)} - \text{(ii)} \\ & = 426 - 91 - 126 \\ & = 391 \text{ mhos cm}^2. \end{aligned}$$

8.8. IONIC EQUILIBRIUM

In 1888, Ostwald pointed out that in a solution of weak electrolyte, there exists an equilibrium between the ions and undissociated molecules. He applied law of mass action to the electrolytic dissociation. Let us consider a solution containing one mole of a simple binary weak electrolyte AB (i.e., one in which each molecule dissociates into two ions in solution) in 'V' litres of solution. Let 'x' be the degree of dissociation (i.e., the fraction of electrolyte dissociated into ions). Then, provided the solution is kept at constant temperature, we can apply the law of mass action to the equilibrium between AB and its ions (A^{+} , B^{-}) by taking the active mass of each ion to be its ionic concentration.

	AB	\rightleftharpoons	A^{+}	B^{-}
Initial	1 mole		0	0
At equilibrium	(1-x) mole		x mole	x mole
Concentration at equilibrium	$\frac{(1-x)}{V}$		$\frac{x}{V}$	$\frac{x}{V}$

\therefore By the law of mass action.

$$\frac{[\text{A}^{+}] \cdot [\text{B}^{-}]}{[\text{AB}]} = \text{Constant, at constant temperature.}$$

$$\text{or } \frac{\frac{x}{v} \cdot \frac{x}{v}}{\frac{(1-x)}{v}} = K \text{ (constant).}$$

$$\text{or } \frac{x^2}{(1-x)v} = K \text{ (a constant), at constant temperature.}$$

If 'c' is the concentration of AB in gram mole per litre, then

$$\frac{x^2 c}{(1-x)} = K$$

This is a statement in symbols of **Ostwald's dilution law**. The constant K , is known as the *dissociation constant* of the weak electrolyte at that temperature.

For very weak electrolytes 'x' is very small and $(1-x)$ is almost equal to unity and so

$$\begin{aligned} K &\cong x^2 c \\ \text{or } x &\cong \sqrt{K/c} \end{aligned}$$

i.e., the degree of dissociation of a weak electrolyte is inversely proportional to the square root of its concentration.

Example 8.9. A 0.01M solution of binary electrolyte dissociates to the extent of 10%. Calculate its dissociation constant.

Here $x = 10\%$ or 0.1 ; $c = 0.01$

$$\begin{aligned} \therefore K &= \frac{x^2 c}{(1-x)} = \frac{(0.1)^2 \cdot (0.01)}{(1-0.1)} = \frac{0.01 \times 0.01}{0.9} \\ &= 1.11 \times 10^{-4} \end{aligned}$$

Example 8.10. The dissociation constant of acetic acid at 298K is 1.8×10^{-5} . Calculate the degree of dissociation of 0.01M solution of acid.

$$\text{We have } K = \frac{x^2 c}{(1-x)} \cong x^2 c.$$

Substituting $K = 1.8 \times 10^{-5}$; $c = 0.01$, we get

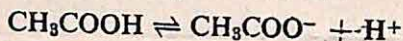
$$1.8 \times 10^{-5} = x^2 \times 0.01$$

$$\text{or } x^2 = \frac{1.8 \times 10^{-5}}{0.01} = 1.8 \times 10^{-3}$$

$$\begin{aligned} \text{or degree of dissociation, } x &= (1.8 \times 10^{-3})^{\frac{1}{2}} \\ &= 4.25 \times 10^{-2} \text{ or } 4.25\% \end{aligned}$$

Example 8.11. The dissociation constant of acetic acid is 1.85×10^{-5} at 298K. Calculate the approximate hydrogen ion concentration in an 0.1N solution of acetic acid.

Dissociation of acetic acid is represented as :



Initial	1 mole	0	0
At equilibrium	(1-x)	x g-ion	x g-ion
Concentration	(1-x) c	xc	xc

From Ostwald's dilution law

$$K = \frac{(xc) \cdot (xc)}{(1-x)c} = \frac{x^2 c}{1-x} \cong x^2 c.$$

Here $c=0.1$; $K=1.85 \times 10^{-5}$

$$1.85 \times 10^{-5} = x^2 (0.1)$$

$$\therefore x^2 = 1.85 \times 10^{-5} = 1.85 \times 10^{-4}.$$

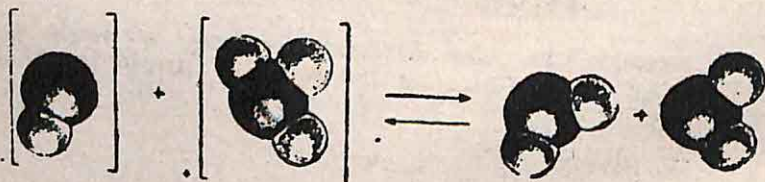
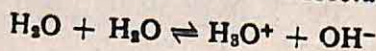
$$\text{or } x = 0.0135 \text{ or } 1.35\%.$$

$$\text{Now } (\text{H}^+) = xc = 0.135 \times 0.1 = 1.35 \times 10^{-3}.$$

Thus the concentration of hydrogen ion in the solution is 1.35×10^{-3} g-ion per litre.

8.9. DISSOCIATION OF WATER

If water is purified by repeated distillation (or by using a mixture of ion-exchange resins) its equivalent conductance falls to a steady very low value. *That this slight conductance remains, no matter how many times the water is distilled, shows that water, however pure it may be, always contains some ions, which are believed to be formed as a result of its own dissociation.*



or more simply $\text{H}_2\text{O} \rightleftharpoons \text{H} + \text{OH}^-$

Applying the law of mass action to this equilibrium at constant temperature and taking the concentrations of the ions expressed in gram-ion per litre as their active masses, we get,

$$\frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \text{Constant, } (K).$$

$$\text{or } [\text{H}^+][\text{OH}^-] = K \times [\text{H}_2\text{O}].$$

Now $[\text{H}_2\text{O}]$, which is the molar concentration of undissociated water molecules in water, is effectively constant since water is an

extremely weak electrolyte and is only very slightly dissociated into ions. Hence, $[H_2O]$ is constant.

$$\therefore [H^+][OH^-] = K \times \text{constant} \\ = K_w \text{ (at constant temperature)}$$

where the constant, K_w is known as the *ionic product of water*.

Since each molecule of water gives rise to one hydrogen ion and one hydroxyl ion when it dissociates, the concentration of these two ion must necessarily be the same in pure water. Experiment shows that this concentration is about 10^{-7} mole/litre at 298K.

$$\text{i.e., } [H^+] = [OH^-] = 1 \times 10^{-7} \text{ mole/litre.}$$

\therefore Ionic product of water at 228K is given by

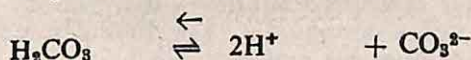
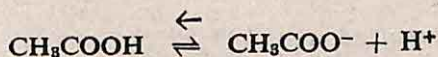
$$K_w = [H^+][OH^-] = 1 \times 10^{-7} \times 1 \times 10^{-7} \\ = 1 \times 10^{-14} \text{ mole/litre.}$$

8.10. ACID-BASE EQUILIBRIUM

According to Arrhenius theory of electrolytic dissociation, *acidity is due to hydrogen ions, H^+ ; and alkalinity is due to hydroxyl ions, OH^-* . The strength of an acid (or base), therefore, is measured by the degree to which it dissociates into hydrogen ions (or hydroxyl ions) in aqueous solution. Thus, hydrochloric acid and nitric acid are described as **strong acids** because they are *largely dissociated in aqueous solution*,

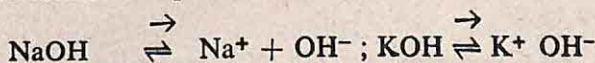


whilst acetic acid and carbonic acid are said to be **weak acids** because their dissociation is small in aqueous solution.

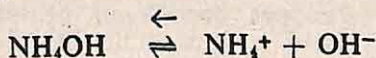


Here arrow above reversible arrow indicates the direction in which the ionic equilibria greatly predominates.

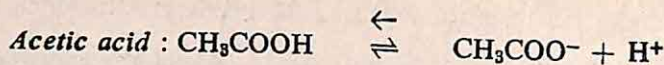
In the same way, alkalis such as sodium hydroxide and potassium hydroxides are called **strong bases** because they are *largely dissociated in aqueous solutions*:



and ammonium hydroxide is said to be a **weak base** because of its *rather slight dissociation*.



The relative strengths of weak acids (and bases) can be easily compared in terms of their dissociation constants at the same temperatures as follows:



$$K = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]} = 1.85 \times 10^{-5} \text{ at } 298\text{K}$$

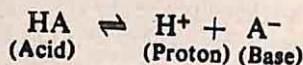


$$K = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]} = 7.2 \times 10^{-10} \text{ at } 298\text{K}.$$

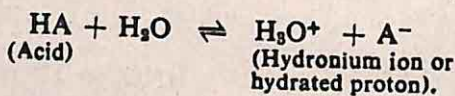
Thus, acetic acid is much stronger than prussic acid.

The above Arrhenius concept of acids and bases has undergone a fundamental change. According to the "modern views by Lowry and Bronsted"

(i) An acid is any molecule or ion which can give a proton to another molecule or ion; and the substance which can combine with a proton is described as the base. In other words, *acid is a proton-donor; while a base is a proton-acceptor*. Accordingly, acids and bases are related as indicated by



(2) In order for an acid to act as a proton donor, a proton acceptor must be present to receive the proton. The proton acceptor in aqueous solution is water.

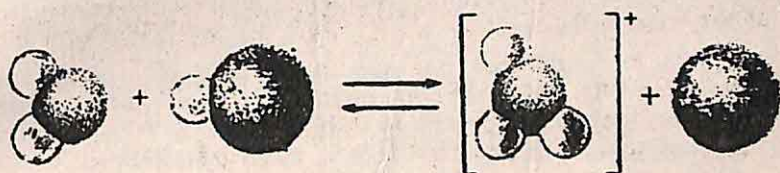
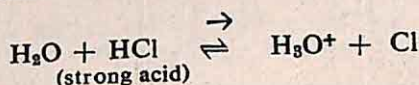


Thus, *hydronium ions* are formed when the acid, HCl, gives up its proton to a water.

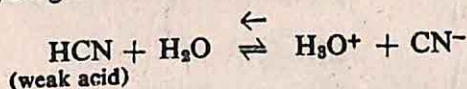
(3) Acids are classified according to the number of protons donated per molecule in aqueous solution. If 1 proton is donated per molecule, the acid is *monoprotic*; 2 protons per molecule, the acid is *diprotic*; 3 protons per molecule, the acid is *triprotic* and so on. The terms *monobasic*, *diabasic* and *tribasic* are used occasionally as synonyms for monoprotic, diprotic and triprotic respectively. Similarly, bases are classified according to their ability to add protons in aqueous solution. If 1 proton is added per molecule, the base is *monoacid base*; 2 protons per molecule, a *diacid base*; and so on.

(4) Acids are commonly classified according to their ability to donate protons, when added to water to yield a dilute solution (0.1M or less). A proton donor is classed as "*strong acid*" if all of its molecule apparently disappear because of proton donation, when they are added to yield a dilute solution. For example, hydrogen chloride is a strong acid, because, if 0.01 mole is added to water to yield 1 litre of solution, the hydrogen ion concentration

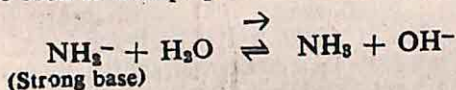
is nearly 0.01 molar.



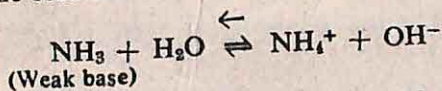
On the other hand, a proton donor is called a '*weak acid*' if it is incompletely dissociated, when added to water to yield a dilute solution. For example, hydrogen cyanide is a weak acid, because, if 0.01 mole is added to water to yield 1 litre of solution, the hydrogen ion concentration is much less than 0.01 molar.



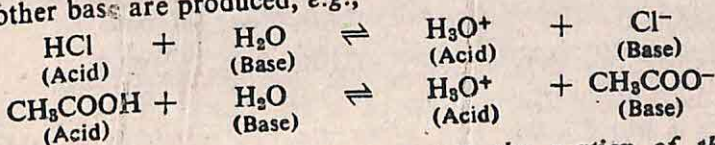
Similarly, *bases* are commonly classified according to their ability to accept protons when added in water to yield dilute solution. A base is classed as '*strong*' if all of its molecules accept at least one proton, when the base is added to water to yield a dilute solution. For example, amide ion is a strong base, because when it is added to water to yield a dilute solution; most of the amide ions are seen to accept protons from water molecules.



On the other hand, a base is said to be '*weak*' if its molecules are only partially protonated when added to water to yield a dilute solution. For example, ammonia is a weak base, because when it is added to water a larger fraction of unprotonated molecules exist in the solution.

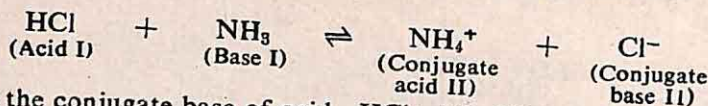


(5) Whenever an acid reacts with a base, another acid and another base are produced, e.g.,



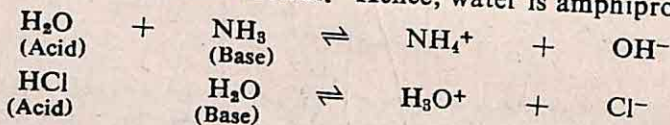
(6) When an acid donates a proton, the portion of the acid that remains is the conjugate base of the acid. On the other hand,

when a base accepts a proton, the entity so produced is the conjugate acid of the base. For example, in the following acid-base reactions,

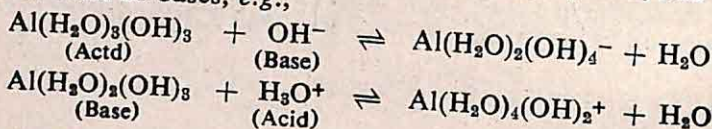


Cl^- is the conjugate base of acid, HCl while NH_4^+ is the conjugate acid of the base, NH_3 .

(7) If a molecule can act both as an acid and as base in aqueous solution it is said to be amphiprotic" (or amphoteric). For example, water may lose a proton to a base, such as NH_3 , or gain a proton from acid, such as HCl . Hence, water is amphiprotic.

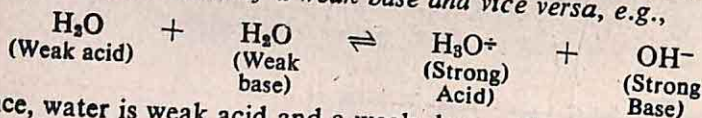


Similarly, hydroxides of certain metals are amphiprotic, and react either as acids or bases, e.g.,



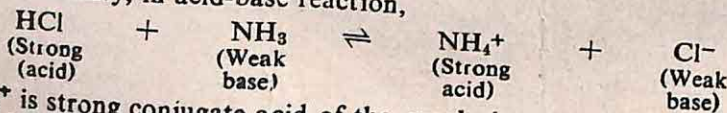
(8) Every acid has at least one covalently bound proton (Usually attached to either oxygen, or nitrogen, or a halogen kernel) and every base has at least one unshared pair of electrons.

(9) The conjugate acid of a strong base is always weaker acid than the conjugate acid of a weak base and vice versa, e.g.,



Hence, water is weak acid and a weak base. Consequently, hydronium ion (H_3O^+) is a strong acid; and hydroxyl ion (OH^-) is a strong base.

Similarly, in acid-base reaction,



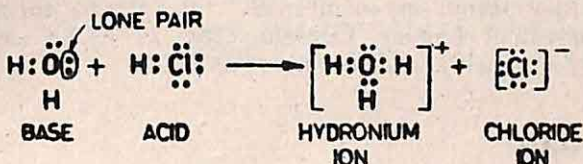
NH_4^+ is strong conjugate acid of the weak base, NH_3 ; and Cl^- is weak base of strong acid, HCl .

(10) The hydrated proton, H_3O^+ or H^+ (aq), is the strongest acid that can exist in dilute aqueous solution; and hydroxide ion OH^- is the strongest base that can exist in dilute solution.

3.11. LEWIS CONCEPTS OF ACIDS AND BASES

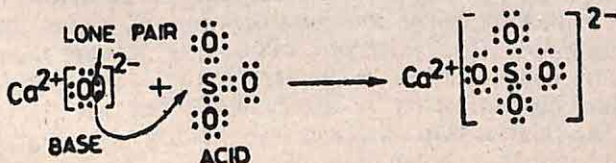
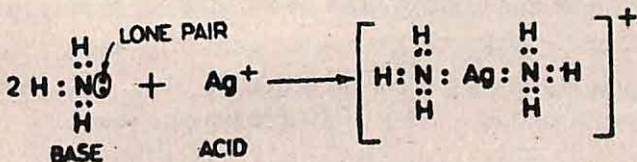
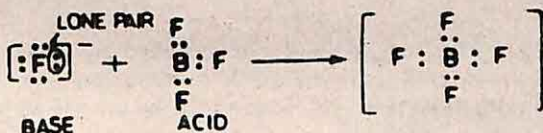
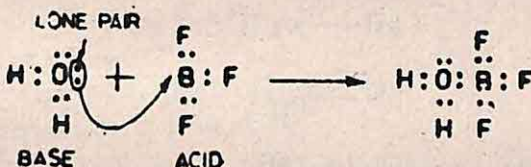
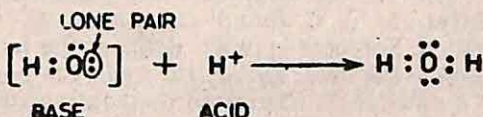
In 1923, 'G.N. Lewis proposed a generalised theory of acids and bases in which acids and bases are not restricted to proton

donors and proton acceptors respectively. According to the *Lewis theory* "an acid is any species (molecular or ion) which can donate a pair of electrons." Consequently, an acid-base reaction consists of the donation of a pair of electrons from the base to the acid with the formation of a co-ordinate bond between the two. For example, in the reaction,



the oxygen atom of the molecule donates an electron pair for the formation of a co-ordinate bond with the hydrogen of the hydrogen chloride molecule. Hence, water is the Lewis base and hydrogen chloride is the Lewis acid.

The following equations show the more general applications of the acid base theory as proposed by Lewis.



One distinct advantage of the Lewis theory is that it explains the long-recognised basic properties of metal oxides (like CaO) and the acidic properties of non-metal oxides like (SO_3), as illustrated in the last reaction.

Thus, according to Lewis, *an acid is an electronically deficient entity* and it may accept one or more electron pairs to form one or more new covalent bonds. Consequently, *an entity which is electronically satisfied cannot behave as an acid.*

8.12. pH VALUE

The concentration of the hydrogen ion is a measure of acidity or alkalinity of a solution, since the hydroxyl ion concentration can always be deduced from the relationship.

$$[\text{OH}]^- = \frac{K_w}{[\text{H}^+]} = \frac{10^{-14} \text{ at } 298\text{K}}{[\text{H}^+]}$$

Now in view of the wide variation which is possible in the H^+ ion concentration, it is found convenient to express it on a logarithmic scale. S. Sorensen (1909) defined the term "*pH as the negative logarithm to the base 10 of the hydrogen ion concentration in mole/litre of a solution.*" Expressed mathematically, we have

$$\text{pH} = -\log (\text{H}^+)$$

$$\text{or} \quad \text{pH} = \log \frac{1}{(\text{H}^+)}$$

$$\text{and} \quad (\text{H}^+) = 10^{-\text{pH}}$$

Thus, *pH value is "the negative power to which 10 must be raised to express the hydrogen ion concentration"*. Consequently, higher the hydrogen ion concentration, the lower will be its pH value.

We know that ionic product of water at 298 K is 1×10^{-14}

$$\text{i.e., } K_w = [\text{H}^+] \times [\text{OH}^-] = 1 \times 10^{-14} \text{ (at } 298 \text{ K)}$$

$$\text{Also in pure water } [\text{H}^+] = [\text{OH}^-]$$

$$\therefore \text{ In neutral solution } [\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$$

Consequently, *pH of natural solution is 7. In acidic solution, is less than 7* since hydrogen ion concentration is higher than 10^{-7} . On the other hand, *pH of alkaline solution is greater than 7* since hydroxyl ion concentration is greater than 10^{-7} and therefore, the hydrogen ion concentration is less than 10^{-7} because $[\text{H}^+] \times [\text{OH}^-] = 10^{-14}$. The relationship between the acidity or alkalinity of a solution and its pH is shown diagrammatically in Fig. 8.8.

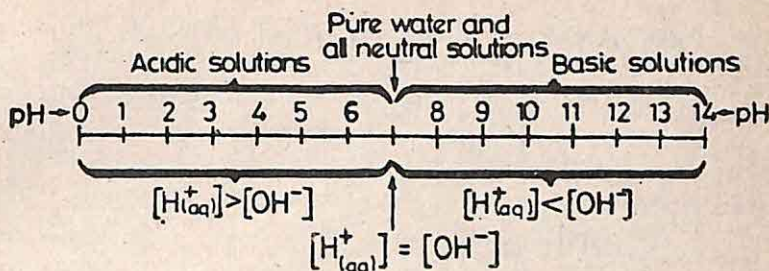


Fig. 8.8. The pH scale.

Example 8.12. Calculate the hydrogen ion concentration of a solution whose pH is 4.4.

$$\begin{aligned} \text{pH} &= -\log [H^+] = 4.4 \\ \text{or } \log [H^+] &= -4.4 = 0.6 - 5.0 \\ [H^+] &= \text{Antilog of } (0.6 - 5) \\ &= (\text{Antilog of } 0.6) \times (\text{Antilog of } -5) \\ &= 4 \times 10^{-5} \text{ M.} \end{aligned}$$

Example 8.13. Calculate the hydroxyl ion concentration of a solution whose pH is 9.

$$\begin{aligned} \text{pH} &= -\log [H^+] = 9 \\ \text{or } \log [H^+] &= -9 \\ [H^+] &= \text{Antilog of } (-9) = 10^{-9} \text{ M.} \\ \text{But } [H^+][OH^-] &= 1 \times 10^{-14} \\ \therefore [OH^-] &= \frac{1 \times 10^{-14}}{10^{-9}} = 10^{-5} \text{ M.} \end{aligned}$$

Example 8.14. Calculate the pH of 0.01M HCl solution, assuming HCl to be completely ionised.

Since HCl is supposed to be completely ionised in 0.01M solution, so, $[H^+] = 0.01 \text{ M} = 10^{-2} \text{ M}$

$$\text{or } \text{pH} = -\log [H^+] = -\log 10^{-2} = -(-2) = 2.$$

Example 8.15. Calculate the pH 0.005M HNO_3 , assuming nitric acid to be completely ionised.

$$\begin{aligned} \text{In } 0.005 \text{ M, } \text{HNO}_3 \text{H}^+ &= 0.005 \text{ M} = 5 \times 10^{-3} \text{ M} \\ \therefore \text{pH} &= -\log [H^+] = -\log (5 \times 10^{-3}) \\ &= -(\log 5 + \log 10^{-3}) \\ &= -(0.699 - 3.0) \\ &= -(-2.301) \\ &= 2.301. \end{aligned}$$

Example 8.15. Calculate the pH of 0.0001M NaOH, assuming it to be completely ionised.

In 0.0001M NaOH, $[\text{OH}^-] = 0.0001\text{M} = 10^{-4}\text{M}$

$$\text{But } [\text{H}^+] = \frac{1 \times 10^{-14}}{[\text{OH}]}$$

$$\therefore [\text{H}^+] = \frac{1 \times 10^{-14}}{1 \times 10^{-4}} = 10^{-10}$$

$$\therefore \text{pH} = -\log (\text{H}) = -\log 10^{-10} \\ = -(-10) = 10,$$

Example 8.16. Calculate the pH of 0.1M acetic acid, which is 1.34 percent ionised.

The $[\text{H}^+]$ of this weak acid $= 0.1\text{M} \times 0.0134 = 1.34 \times 10^{-3}\text{M}$.

$$\therefore \text{pH} = -(\log [\text{H}^+] = -\log (1.34 \times 10^{-3}) \\ = -(\log 1.34 + \log 10^{-3}) \\ = -(0.13 - 3.00) \\ = -(-2.87) \\ = 2.87.$$

Example 8.17. The dissociation constant of a weak monobasic acid is 1.04×10^{-5} at 298K. Calculate the pH of 0.05M solution of the acid at this temperature.

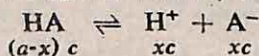
From Ostwald's dilution law, we have degree of dissociation.

$$x = \sqrt{K/c}$$

$$\text{But } c = 0.05 \text{ M} : K = 1.04 \times 10^{-5}$$

$$\therefore x = \sqrt{\frac{1.04 \times 10^{-5}}{0.05}} = 0.0144.$$

Now for monobasic acid, H.A.



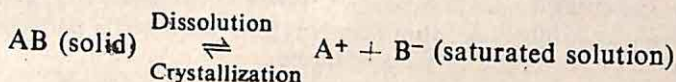
we have,

$$[\text{H}^+] = xc \\ = 0.0144 \times 0.05 \\ = 0.00072 \text{ M.} \\ = 7.2 \times 10^{-4} \text{ M.}$$

$$\therefore \text{pH} = -\log [\text{H}^+] \\ = -\log (7.2 \times 10^{-4}) \\ = -(\log 7.2 + \log 10^{-4}) \\ = -(0.853 - 4.0) \\ = -(-3.142) \\ = 3.142.$$

8.13. SOLUBILITY PRODUCT CONSTANT.

A slightly or sparingly soluble electrolyte (like Ag^+Cl^- , $\text{Pb}^{2+}\text{SO}_4^{2-}$, $\text{Ba}^{2+}\text{SO}_4^{2-}$, $\text{Pb}^{2+}\text{Cl}_2^-$, $\text{Ag}_2+\text{CrO}_4^{2-}$ dissolves in water to a small extent and it forms a saturated solution. *In a saturated solution, an equilibrium exists between the dissolved ions and undissolved solute, i.e., the rate at which ions leave the solid salt and pass into solution is equal to the rate at which ions return to the solid solute from solution.* Let us consider a saturated solution of a binary electrolyte AB in contact with an excess of undissolved solid at constant temperature. The following equilibrium is set up.



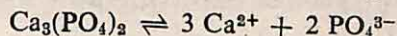
Applying the law of mass action to this system, and taking the concentration of the individual ions as their active masses, we get the mathematical expression.

$$\frac{[\text{A}^+][\text{B}^-]}{[\text{AB solid}]} = \text{Constant.}$$

Now the active mass of any solid is a constant at constant temperature, so $[\text{AB solid}]$ is constant,

$$\therefore [\text{A}^+][\text{B}^-] = \text{Constant} = K_s$$

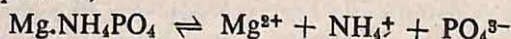
where K_s is called the **solubility product constant**, or sometime simply the solubility product of the electrolyte AB at that temperature. Thus, "*in a saturated solution of a slightly soluble electrolyte the product of the molar concentration of its ions is constant at a given temperature if the two kinds of ions are formed in equal numbers.*" If the electrolyte gives more than one ion of one kind in solution, the concentration of that ion must be raised to the corresponding power when stating the solubility product. For, example, calcium phosphate dissociates according to the equation.



so, the expression for its solubility products constants is

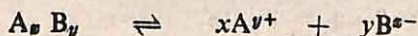
$$[\text{Ca}^{2+}]^3 \times [\text{PO}_4^{3-}]^2 = K_s$$

For a salt like magnesium ammonium phosphate, which dissociates according to the equation,



we have $[\text{Mg}^{2+}] \times [\text{NH}_4^+] \times [\text{PO}_4^{3-}] = K_s$.

Similarly, for a general electrolyte A_xB_y , which dissociate thus,



the solubility product is given by

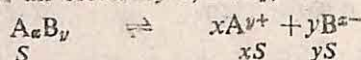
$$K_s = [\text{A}^{y+}]^x [\text{B}^{x-}]^y$$

Consequently, the **solubility product constant** of a sparingly soluble electrolyte may be defined as *"the product of the concentrations of its constituent ions raised to appropriate powers, in a saturated solution."* It is a constant for the electrolyte at constant temperature, like a normal equilibrium constant.

Applications of solubility product. The concept of solubility product has been very helpful in studying the reactions involving ionic equilibria. Some of the more important applications of solubility product principle are :

(1) **Calculation of solubility.** When the solubility product constant for a slightly soluble electrolyte is known, its solubility in moles per litre, can readily be calculated.

Similarly, the solubility product of an electrolyte can be calculated from its solubility. Suppose S is the solubility (in gram mole per litre) of an electrolyte, A_xB_y , which dissociates as :



Since 1 molecule of A_xB_y gives x and y -ions of A^{y+} and B^{x-} respectively. So, molar concentrations of A^{y+} and B^{x-} are given by :

$$[A^{y+}] = xS, [B^{x-}] = yS$$

$$\begin{aligned} \therefore K_s &= [A^{y+}]^x \cdot [B^{x-}]^y \\ &= (xS)^x \cdot (yS)^y \\ &= x^x \cdot y^y \cdot S^{x+y} \end{aligned}$$

For example, in case of $BaSO_4$, which dissociates as .



$$x=1, y=1,$$

$$\therefore K_s = 1 \times 1 (S)^{1+1} = S^2.$$

For an electrolyte like Ag_2CrO_4 , which dissociates according to equation,



$$x=2, y=1,$$

$$\therefore K_s = 2^2 \times 1^1 \times S^{2+1} = 4S^3.$$

2. Predicting ionic reactions. The importance of solubility product constant is that it indicates the maximum value of the ionic product in a solution. In other words, if the ionic product of an electrolyte exceeds its solubility product even momentarily, the excess ions immediately combine and the solid salt is precipitated out, i.e.,

Ionic product $> K_s$, precipitation takes place.

Thus, when equal volume of 2×10^{-4} M solution of $AgNO_3$ and 2×10^{-4} solution of $NaCl$ are mixed, we can show that silver chloride will precipitate. Because the volume is doubled by mixing equal volumes of the two solutions, concentration of each ion is

reduced to half its initial value, consequently, molar concentration of both ions

$$[\text{Ag}^+] = [\text{Cl}^-] = \frac{2 \times 10^{-4} \text{M}}{2} = 1 \times 10^{-4} \text{M}$$

immediately on mixing the two solutions. So, ionic product,

$$[\text{Ag}^+] \cdot [\text{Cl}^-] = 1 \times 10^{-4} \times 1 \times 10^{-4} = 1 \times 10^{-8} > K_s.$$

because $K_s = [\text{Ag}^+] [\text{Cl}^-] = 1.7 \times 10^{-10}$.

So we see that, momentarily, the ionic product is greater than K_s for AgCl. According to the principle of chemical equilibrium, some

Table 8.2. Solubility Product (K_s) at Room Temperature.

Substance	K_s	Substance	K_s
Silver bromide	5×10^{-13} ;	Manganese sulphide	8×10^{-14}
Silver chloride	1.7×10^{-10} ;	Zinc sulphide	1×10^{-20}
Silver iodide	8.5×10^{-17} ;	Nickel sulphide	1×10^{-22}
Barium sulphate	1.5×10^{-9} ;	Cobalt sulphide	5×10^{-22}
Lead sulphate	1.3×10^{-8} ;	Lead sulphide	4×10^{-26}
Lead chloride	1.7×10^{-5} ;	Cadmium sulphide	6×10^{-27}
Copper carbonate	2.5×10^{-10} ;	Bismuth sulphide	6×10^{-70}
Calcium carbonate	7×10^{-9} ;	Copper sulphide	4×10^{-36}
Aluminium hydroxide	5×10^{-33} ;	Mercuric sulphide	1×10^{-50}
Chromium hydroxide	7×10^{-31} ;	Magnesium hydroxide	9×10^{-12}
Cobalt hydroxide	1×10^{-43} ;	Zinc hydroxide	3×10^{-27}
		Ferric hydroxide	6×10^{-38}

of the silver and chloride ions will unite under these conditions with the formation of solid silver chloride, and the precipitation will continue until the product of $[\text{Ag}^+]$ and $[\text{Cl}^-]$ still remaining in the solution attains a value equal to the solubility product constant for silver chloride.

(3) **Qualitative analysis.** The theory of the solubility product gives an interesting explanation of many of the reactions used in qualitative analysis. In I group, Pb^{2+} , Ag^+ and Hg_2^{2+} ions are precipitated as their chlorides by adding dilute hydrochloric acid to a cold aqueous solution, since the solubility products of these chlorides is low. In presence of large concentration of chloride ion (from the added hydrochloric acid) the ionic product, exceeds the solubility product of these metal chlorides and hence they are thrown out as precipitate.

Example 8.18. The solubility of BaSO_4 in water is 2.42×10^{-3} gram per litre at 298K. Calculate the solubility product constant for BaSO_4 . (At. mass of Ba=137, S=32, O=16).

First calculate the molar solubility of BaSO_4 . The molecular mass of $\text{BaSO}_4 = 137 + 32 + 64 = 233$.

$$\therefore \text{Solubility, } S = \frac{2.42 \times 10^{-3} \text{ g/litre}}{233 \text{ g/mole}} \\ = 1.04 \times 10^{-5} \text{ mole/litre.}$$

Since BaSO_4 dissolves to give Ba^{2+} and SO_4^{2-} in equal numbers,

$$\begin{aligned} \text{BaSO}_4 &\rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-} \\ \text{so, } [\text{Ba}^{2+}] &= [\text{SO}_4^{2-}] = S = 1.04 \times 10^{-5} \text{ M} \\ \therefore K_s &= [\text{Ba}^{2+}] \cdot [\text{SO}_4^{2-}] \\ &= (1.04 \times 10^{-5}) \cdot (1.04 \times 10^{-5}) \\ &= 1.08 \times 10^{-10}. \end{aligned}$$

Example 8.19. Calculate the solubility product constant for silver chromate whose molar solubility is 1.3×10^{-4} at 298K.

Writing the equation for the dissociation of Ag_2CrO_4 ,



we see that concentration of silver ion is twice the molar solubility of Ag_2CrO_4 , and that the concentration of chromate ion is equal to the molar solubility of the salt, so that $[\text{Ag}^+] = 2 \times 1.3 \times 10^{-4} \text{ M}$; and $[\text{CrO}_4^{2-}] = 1.3 \times 10^{-4} \text{ M}$. Substituting in the expression for the solubility product, we get.

$$\begin{aligned} \therefore [\text{Ag}^+]^2 \cdot [\text{CrO}_4^{2-}] &= K_s \\ \text{or } (2 \times 1.3 \times 10^{-4})^2 \cdot (1.3 \times 10^{-4}) &= K_s \\ \text{or } K_s &= 9.8 \times 10^{-12}. \end{aligned}$$

Example 8.20. The solubility product constant for silver chloride is 1.2×10^{-10} at 298K. Calculate the molar solubility of silver chloride at 298K.

Silver chloride dissociates according to the equation.



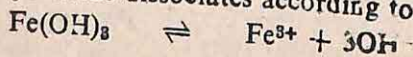
Let S be the solubility of AgCl in moles per litre. Consequently, the molar concentration of Ag^+ and Cl^- will also be S each. Substituting in the expression for solubility product constant of AgCl , we have

$$\begin{aligned} [\text{Ag}^+] \cdot [\text{Cl}^-] &= K_s = 1.2 \times 10^{-10} \\ \text{or } S \times S &= 1.2 \times 10^{-10} \\ \text{or } S &= \sqrt{1.2 \times 10^{-10}} = 1.1 \times 10^{-5} \text{ mole/litre.} \end{aligned}$$

Hence, the molar solubility of silver chloride is 1.1×10^{-5} .

Example 8.21. The solubility product constant of $\text{Fe}(\text{OH})_3$ is 1.1×10^{-36} . Calculate the molar solubility of iron (III) hydroxide.

Iron (III) hydroxide dissociates according to the equation.



Let S be the molar solubility of salt. It is apparent from the above equation that each mole of $\text{Fe}(\text{OH})_3$ that dissolves yields one mole of Fe^{3+} and three moles of OH^- . Thus, if the molar solubility of $\text{Fe}(\text{OH})_3$ is S , then

$$[\text{Fe}^{3+}] = S, \text{ and } [\text{OH}^-] = 3S.$$

Substituting these values in the expression for the solubility product constant for ferric hydroxide, we have

$$[\text{Fe}^{3+}] [\text{OH}^-]^3 = K_s = 1.2 \times 10^{-36}$$

$$\text{or } S(3S)^3 = 1.1 \times 10^{-36}$$

$$\text{or } 27S^4 = 1.1 \times 10^{-36}$$

$$\text{or } S^4 = \frac{1.1 \times 10^{-36}}{27} = 407 \times 10^{-40}$$

$$\text{or } S = 4.5 \times 10^{-10} \text{ mole/litre.}$$

Hence, the molar solubility of ferric hydroxide is 4.5×10^{-10} .

Example 8.22. *Equal volumes of $1 \times 10^{-2} \text{ M}$ calcium chloride and $4.0 \times 10^{-4} \text{ M}$ sodium sulphate solution are mixed. Show whether a precipitate of calcium sulphate will be formed or not? Solubility product constant of calcium sulphate is 2.4×10^{-5} .*

On mixing equal volumes of $1 \times 10^{-2} \text{ M}$ CaCl_2 and $4.0 \times 10^{-4} \text{ M}$ Na_2SO_4 , the concentration of each is reduced to half its initial value.

$$\therefore [\text{Ca}^{2+}] = \frac{1}{2} \times 1 \times 10^{-2} \text{ M} = 0.5 \times 10^{-2} \text{ M}$$

$$\text{and } [\text{SO}_4^{2-}] = \frac{1}{2} \times 4 \times 10^{-4} \text{ M} = 2 \times 10^{-4} \text{ M}$$

$$\therefore \text{Ionic product, } [\text{Ca}^{2+}] [\text{SO}_4^{2-}] = (0.5 \times 10^{-2}) \times (2 \times 10^{-4}) \\ = 1 \times 10^{-6}.$$

Since ionic product, ($= 1 \times 10^{-6}$) is less than its solubility product ($= 2.4 \times 10^{-5}$) so, *no precipitation of calcium sulphate will take place.*

8.14. COMMON ION EFFECT

Consider the equilibrium existing in a solution of a weak binary electrolyte, AB



\therefore On applying law of mass action, we get

$$K = \frac{[\text{A}^+] \cdot [\text{B}^-]}{[\text{AB}]}$$

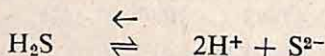
Now if to this solution a strong electrolyte AC or BD having a common ion A^+ or B^- is added. Due to the ionization of AC



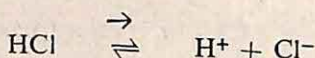
the concentration of A^+ will be increased. In order to keep K constant the concentration of B^- will decrease and that of AB will

increase. In other words, more AB molecules will be formed, i.e., the degree of dissociation of AB will be suppressed. *This process of decreasing ionization of a weak electrolyte by the addition of a strong electrolyte having an ion common with the weak electrolyte, is known as common ion effect,*

Applications of common ion effect. (i) *In analytical chemistry.* In II group of qualitative analysis, the ionisation of weak acid H_2S

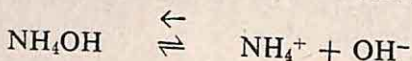


is suppressed by the presence of strong acid, HCl , having a common ion H^+ .

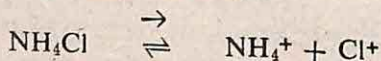


Due to the suppressed degree of dissociation of H_2S , the concentration of S^{2-} ions produced is low, which causes the precipitation of sulphide of II group cations only, since the solubility product of these sulphides is comparatively high.

Similarly, in III group, the ionisation of weak base NH_4OH ,



is suppressed by the prior addition of NH_4Cl which furnishes a high concentration of common ion NH_4^+ .



Due to this low dissociation of NH_4OH , the OH^- concentration is quite low. This low OH^- ion concentration is sufficient only to precipitate hydroxides of Al^{3+} , Cr^{3+} and Fe^{3+} .

(ii) *Purification of common salt.* NaCl , as obtained from natural sources, is usually contaminated with small amounts of deliquescent impurities like CaCl_2 and MgCl_2 . The purification of chloride solution is effected by passing HCl gas into a saturated solution of the impure sodium chloride. The addition of HCl (containing Cl^-) causes the precipitation of only NaCl , but impurities remain in solution since the solution is not saturated so far as calcium and magnesium chlorides are concerned.

(iii) *Salting out of soap.* In the soap manufacture, a solution of common salt is added to solution of soap (sodium stearate) to obtain solid soap. Addition of common salt (NaCl) increases the value of $(\text{Na}^+) \times (\text{Stearate}^-)$ in solution until the solubility product of soap is exceeded, whereby soap gets precipitated.

(iv) *In gravimetric analysis.* When excess of precipitant (HCl or H_2SO_4) is added to solution containing Ag^+ or Ba^{2+} ions, complete precipitation of AgCl or BaSO_4 occurs due to the presence of excess of common ion Cl^- or SO_4^{2-} .

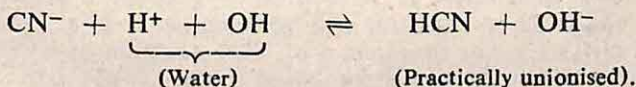
8.15. HYDROLYSIS

When a salt is added to water, the solution may remain neutral or it may become acidic or basic, depending upon the type of salt. In pure water the H^+ and OH^- ions are equal in number. If one or more of ions of the added salt react either with the ions of water (*i.e.*, H^+ or OH^-) their equality may be destroyed and the solution may become acidic or basic. If such a reaction occurs, the salt is said to be hydrolysed. **Hydrolysis is therefore, the inter-action of salts with the ions of water.**

Salt are usually classified into four types for purposes of studying their hydrolysis. The classes are :

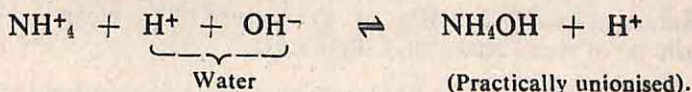
(i) **Salt of strong acid and strong base** *e.g.*, $NaCl$, KNO_3 , etc. This class of salt does not hydrolyse because neither of the salt ions is capable of reacting with either H^+ or OH^- of the water. Thus, if Na^+Cl^- is added to water, there is no tendency for Na^+ ions to react with OH^- ions because Na^+OH^- is completely ionised. Similarly, there is no tendency for Cl^- ions to react with H^+ ions because H^+Cl^- is also completely ionised. Therefore, the proportion of H^+ and OH^- ions in solution remains unchanged. In other word, *aqueous solution of a salt strong acid and strong base is neutral.*

(ii) **Salt of weak acid and strong base** *e.g.*, CH_3COONa , Na_2CO_3 , KCN , etc. Salts of this category hydrolyse to give *alkaline* solutions. For examples, when K^+CN^- is dissolved in water, its ions CN^- react with H^+ ion of water to form practically unionised HCN . As H^+ ions are used in reacting with CN^- ions, the resulting solution will contain an excess of OH^- ions over H^+ ions *Hence, the solution will be alkaline in nature.* This is depicted below.



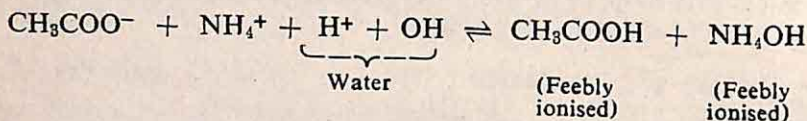
On the other hand, K^+ ions have no tendency to react with OH^- ions because K^+CH^- is completely ionised.

(iii) **Salt of strong acid and weak base**, *e.g.*, $FeCl_3$, NH_4Cl , $C_6H_5NH_3Cl$. Salts of this category undergo hydrolysis to give acidic solutions. For example, when $NH_4^+Cl^-$ is dissolved in water its NH_4^+ ions react with OH^- ions of water to form practically unionised NH_4OH . The other ion, Cl^- , has no tendency to react with H^+ ions (of water) because H^+Cl^- is completely ionised. This hydrolysis reaction is represented as



As OH^- ions of water are used in reaction with NH_4^+ ions of salt, the resulting solution will contain an excess of H^+ over the OH^- ions. *Hence, the solution of NH_4Cl will be acidic in nature.*

(iv) **Salt of a weak acid and weak base** e.g. $\text{CH}_3\text{COONH}_4$, $(\text{NH}_4)_2\text{CO}_3$. Salts of this class undergo hydrolysis to yield either neutral or weak acidic or weak basic solutions. The acidity or alkalinity of the resulting solution depends upon the relative strengths of acid and base formed. For example, when $\text{CH}_3\text{COONH}_4$ is added to water its CH_3COO^- and NH_4^+ ions react with H^+ and OH^- ions of water to form feebly ionised CH_3COOH and NH_4OH . i.e.,



As both CH_3COOH and NH_4OH are nearly equally ionised, so, the resulting solution contains neither excess of H^+ ions nor OH^- ions in solution. Hence, *the solution is almost neutral.*

8.16. BUFFER SOLUTIONS

An aqueous solution of NaCl has a pH of about 7. If 1 ml of 0.1 M HCl solution is added to 1 litre of the NaCl solution, the pH falls to 4. On the other hand, if 1 ml of 0.1 M NaOH solution is added to 1 litre of the solution, the pH would rise to 10. If however, 1 litre aqueous solution of ammonium acetate, which also has a pH of about 7, is treated with 1 ml of 0.1 M HCl or NaOH as above the pH change is negligible. *A solution (such as ammonium acetate) with "reserve" acidity or alkalinity i.e. capable of resisting change of pH when 'small amounts of acid or alkali is added is known as a buffer.*

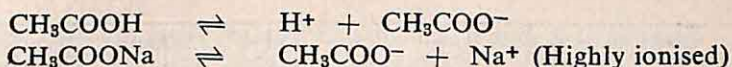
A buffer is used when it is desired to prepare a solution of definite pH and to know that this will not change over a considerable period of time. For example, a M/1000 solution of HCl has a pH of 4, but if left in the bottle for some time, its pH can alter through solution of impurities from the walls of the bottle or from the air. Buffers are of vital importance in biological works (e.g., enzymic studies). For example, in the enzymic degradation of a carbohydrate, such as dextran, by an enzyme dextranase, the complex mixtures of sugars might be ruined if the pH is altered too much from the optimum value (about pH 5.5.). The degradation is therefore, carried out in a buffer of this pH since no pH change takes place. Thus, buffer action is always used when it is desirable to control the pH of a reaction mixture solution within fine limits.

Buffers normally consists of a mixture of a weak acid and their salts or of weak bases and their salts.

(i) *Acid buffer* may be obtained by mixing a weak acid with a salt of the same acid, e.g., $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$.

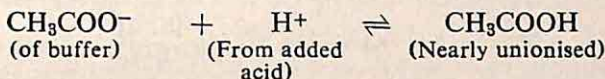
(ii) *Alkaline buffer* may be made by mixing a weak base with a salt of the same weak base, e.g., $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$.

Acidic buffer. A simple buffer can be made from acetic acid and sodium acetate.

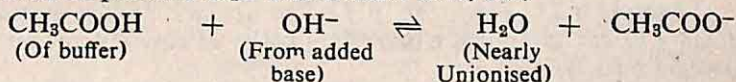


As sodium acetate is fully ionised, the acetate ions so produced suppress the ionisation of the acetic acid so that the mixture contains more unionised acetic acid molecules and more acetate ions than in acetic acid alone.

When a few drops of an acid are added to it, the H^+ ions from the added acid react with excess acetate ions to form feebly (or nearly unionised) acetic acid, *i.e.*,

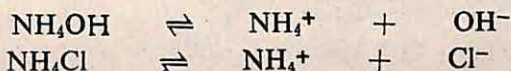


On the other hand, when a few drops of a base (say, NaOH) are added, OH^- of the added base combines with excess acetic acid molecules to produce H_2O and acetate ions, *i.e.*,



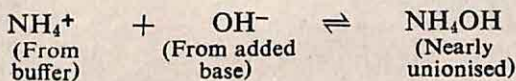
Thus, addition of a small amount of acid or alkali to the buffer solution of sodium acetate and acetic acid does not alter the pH of the mixture to any appreciable extent.

Basic buffer. A mixture of ammonium hydroxide and ammonium chloride provides an example of this class.

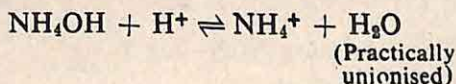


The NH_4^+ ions from the fully ionised NH_4Cl , suppress the ionisation of NH_4OH so that the mixture contains more NH_4OH molecules and more NH_4^+ ions than in ammonium hydroxide alone.

When a few drops of base (say, NaOH) is added to it, the OH^- ions, from the added base, combine with excess NH_4^+ ions to form nearly unionised NH_4OH .



On the other hand, when a few drops of acid (say, HCl) are added, its H^+ ions combines with excess ammonium hydroxide to form nearly unionised water molecules.



Thus, we see that the addition of a small amount of OH^- or H^+ ions to the buffer solution of ammonium hydroxide and ammonium

chloride does not alter the H^+ ion concentration or pH of the mixture.

The pH of a buffer can be calculated from the dissociation constant of the weak acid (or base) and the ratio of the concentration of acid (or base) and its salt present in the mixture, by using **Henderson-Hasselbach equations**.

$$\text{pH of acidic buffer} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\begin{aligned}\text{pH of basic buffer} &= 14 - (-\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}) \\ &= 14 + \log K_b - \log \frac{[\text{Salt}]}{[\text{Base}]}\end{aligned}$$

where K_a (or K_b) is the dissociation constant of weak acid (or weak base).

Example 8.23. Find the pH of an acetate buffer containing 0.01 mole of sodium acetate and 0.1 g mole of acetic acid per litre ($K_a = 1.84 \times 10^{-5}$).

$$\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \text{pH} = -\log 1.84 \times 10^{-5} + \log \frac{0.01}{0.1}$$

$$= -\log 1.84 \times 10^{-5} + \log \frac{0.01}{0.1}$$

$$= -(\log 1.84 + \log 10^{-5}) + \log 10^{-1}$$

$$= -(0.265 - 5.0) + (-1)$$

$$= 3.735.$$

Example 8.24. Calculate the pH of buffer containing 0.1 mole of ammonium chloride and 0.1 mole of ammonium hydroxide per litre ($K_b = 1.84 \times 10^{-5}$).

$$\text{pH} = 14 + \log K_b - \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= 14 + \log 1.84 \times 10^{-5} - \log \frac{0.1}{0.1}$$

$$= 14 + \log 1.84 + \log 10^{-5} - \log 1$$

$$= 14 + 0.265 - 5.0 - 0.$$

$$= 9.265$$

QUESTIONS

(A) Objective Type :

1. (a) How does the conduction of electricity through an aqueous solution of a salt differ from the conduction through a metallic wire?
(b) State Faraday's law of electrolysis.
2. What do you understand by the term "*electrochemical equivalent*" of an element? How is the electrochemical equivalent related to the chemical equivalent of an element?
3. Define specific conductivity and equivalent conductivity of a solution. Describe how you would determine in the laboratory the conductivity of a solution of an electrolyte solution.
4. Explain what is meant by the equivalent conductivity of a solution and describe briefly how this quantity varies with concentration for different types of electrolytes.
5. Define and explain the terms "*specific conductivity*" and "*equivalent conductivity*"; and state how they are related. Draw rough sketches to show how these two quantities vary during the progressive dilution of solutions of (a) sodium chloride, (b) acetic acid.
6. Deduce Ostwald's dilution law for a solution of binary electrolyte.
7. (a) What is meant by the self-ionization of water?
(b) Define pH both in words and by a mathematical equation.
8. What is a buffer solution? How does it function? What is the practical importance of such solutions.
9. What is meant by the term solubility product? Give two examples of the application of this concept.
10. What do you understand by strength of an acid? How is ionisation constant related to its strength?
11. Discuss Bronsted-Lowry concept of acids and bases in detail giving the significance of conjugate acid-base pair.
12. (a) What is meant by "strong" and "weak" acid?
(b) What is Lewis concept of acids and bases?
13. Define the term hydrolysis. Explain why sodium chloride solution is neutral; while that of sodium acetate is alkaline?
14. Explain the following statements.
(a) It is incorrect to refer to concentrated sulphuric acid as "strong sulphuric acid".
(b) On dissolving in water, hydrogen chloride ionises and dissociates but sodium chloride only dissociates.
15. Explain what you understand by (a) the concentration, (b) the strength, (c) basicity, and (d) dissociation constant of an acid.
16. What are the ionic and molecular species present in an aqueous solution of (a) acetic acid, (b) hydrochloric acid?
17. State and explain Kohlrausch's law. How would you determine the conductivity at infinite dilution of acetic acid?

(B) Objective Type :

18. Match the following.

(1) Weak electrolyte	(a) Copper
(2) Strong electrolyte	(b) Acetic acid
(3) Insulator	(c) Sodium chloride
(4) Electronic conductor	(d) Sulphur

19. Match the following :

- | | |
|--|----------------------|
| (1) Electrode at which electrons flow into an electrolyte | (a) Anode. |
| (2) Substance which dissociates readily in solution. | (b) Coulomb. |
| (3) A quantity of electricity. | (c) Cathode. |
| (4) Electrode at which electrons flow out of an electrolyte. | (d) Silver chloride. |
| (5) A substance whose aqueous solution will have a low conductivity. | (e) Electrolyte. |

20. Point out the correct statements.

- (a) An aqueous solution of ammonium chloride would be :
 (i) acidic, (ii) alkaline, (iii) neutral, (iv) a buffer.
- (b) Faraday has the dimensions of (i) coulombs, (ii) coulomb equivalent, (iii) coulombs per equivalent.
- (c) The passage of current in an electrolyte is due to the movement of (i) electrons, (ii) molecules, (iii) atoms, (iv) ions.
- (d) Boron trifluoride is a (i) Lewis acid, (ii) neutral according to Lewis concept.
- (e) The resistance of a metallic conductor (i) increases, (ii) decreases, (iii) remains constant with temperature.
- (f) Ostwald's dilution law is applicable to (i) weak electrolytes, (ii) strong electrolytes, (iii) both.
- (g) The mass of the substance liberated at the electrodes is directly proportional to (i) atomic mass, (ii) molecular mass, (iii) chemical equivalent.
- (h) The cell constant is the product of resistance and (i) specific conductance, (ii) equivalent conductance, (iii) molar conductance.

21. Complete the followings :

- (a) pH is.....logarithm or hydrogen ion concentration of a solution.
- (b) A solution of a salt of weak acid and strong base is.....
- (c) In an acidic solution hydrogen ion concentration is greater thanand the pH of an acidic solution is.....than 7.
- (d) The conjugate base of a weak acid is.....
- (e) An acidic solution has a greater concentration of H^+ ions than OH^- ions, but the product of H^+ and OH^- must be equal to
- (f) The equivalent conductance of an electrolyte.....with dilution.
- (g) Mathematical expression of Ostwald's dilution law is.....

(C) Problems :

22. Calculate the mass of copper deposited from a solution of copper sulphate when a current of 0.75 ampere was passed for 25 minutes. (Chemical equivalent of copper = 31.8).
 (Ans. 0.3705 g.)
23. What is the pH value of (i) 0.01M HCl, (ii) 0.01M NaOH, assuming them fully ionised?
 (Ans. (i) 2.0, (ii) 12.0)
24. Calculate the pH of a 0.01M acetic acid if its dissociation constant is 18×10^{-5} .
 (Ans. 3.37)

25. The pH of a solution is 9.7, what is its hydrogen ion concentration ?
(Ans. 2×10^{-10} mole/litre)
26. Calculate the pH of a buffer solution which is 0.1M each with respect to acetic acid and sodium acetate. The dissociation constant of acetic acid is 1.8×10^{-5} .
(Ans. 4.74).
27. The solubility of BaSO_4 is 1×10^{-5} mole/litre at 298K. Calculate its solubility product.
(Ans. 1×10^{-10})
28. The solubility product of silver chloride is 1×10^{-10} at 298K. Calculate its molar solubility.
(Ans. 1×10^{-5})
29. Lead chloride (PbCl_2) has a solubility product of 1.7×10^{-5} . What is its solubility in moles per litre ?
(Ans. 1.62×10^{-2})
30. A 0.02M solution of ammonium hydroxide is 3% dissociated. Calculate its dissociation constant.
(Ans. 1.8×10^{-5})
31. At 291 K, the equivalent conductances at infinite dilution of NH_4Cl , NaOH and NaCl are 129.5, 217.4 and 108.0 mho cm^2 . Calculate the equivalent conductance at infinite dilution of ammonium hydroxide.
(Ans. 238.3 mhos cm^2)
32. Specific conductance of 0.5M solution of an electrolyte at 298K is 0.02 mhos cm^{-1} . Calculate its molar conductivity.
(Ans. 40 mhos cm^2)

Hydrogen

s - Block (Representative elements)															
Groups I A															
Periods	1	H													
	2	Li	Be												
	3	Na	Mg												
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn
	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb
	7	Fr	Ra	Ac	Ku	Ha									

1. PHYSICAL PROPERTIES

1. Symbol : H.
2. Atomic number : 1.
3. Molecular formula : H_2 ; $H : H$; $H-H$.
4. Atomic mass : 1.008.
5. Electronic structure : $1s^1$.
6. Isotopes : Protium : 1H (99.985%) ; Deuterium 2H (0.015%) ; Tritium 3H (traces).
7. Abundance on earth's crust : 0.88%.
8. Density of gas at STP. : 0.00899 g/l.
9. Density of liquid (at freezing point) : 0.071 g cm^{-3} .
10. Solubility in water (at STP) : 21.5 ml l^{-1} .
11. Melting point : 13.8K.
12. Boiling point : 20.4K.
13. Electronegativity : 2.1
14. Oxidation numbers : +1, -1.
15. Critical temperature : 38.5K.
16. Critical pressure : 12.8 atm.
17. Critical volume : 0.069 l/mole.

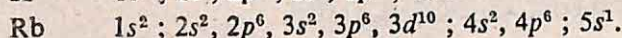
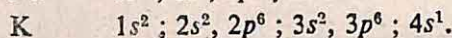
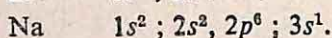
Hydrogen is a colourless, tasteless and odourless gas. Of all the known elements, hydrogen is the lightest. It is the best conductor of heat amongst gases. Because of its lowest density it has the maximum diffusion tendency. Palladium, platinum and some other metals *adsorb** hydrogen. At STP palladium powder may adsorb 900 times its own volume of hydrogen. Adsorbed hydrogen is given out when the metal is heated in vacuum.

1.2. UNIQUE POSITION IN THE PERIODIC TABLE

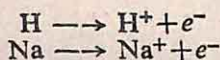
The name hydrogen has been taken from French, hydro—water; gene—producer. It is the lightest of all the elements (atomic mass = 1.008) and its neutral atom consists of a single proton and a single electron, $1s^1$. Thus, on one side it resembles the alkali metals of group IA, which have a single loosely bound electron in outermost orbit (ns^1). On the other hand, it shows an analogy with the halogens of group VIIA (ns^2, np^5), since it is short of one electron than inert gas, helium ($1s^2$). Hydrogen, therefore, occupies unique position in the periodic table. So, an examination of its relationship with alkali metals and with halogen will be of interest.

(A) Resemblance with alkali metal—Electropositive character :

(i) It resembles alkali metals in having a single electron in the valence orbital.



(ii) The removal of an electron converts the hydrogen atom into monovalent hydrogen ion just as a sodium atom is converted into a monovalent sodium cation by the loss of its loosely bound outermost electron :

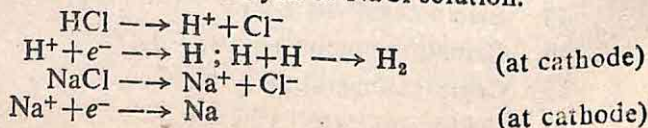


(iii) Because of the formation of H^+ ion, hydrogen is said to possess a valency +1, like sodium, potassium, etc.

(iv) Like alkali metals, hydrogen has great affinity for non-metals and produces compounds such as HCl , HBr , HI , H_2S , etc., similar to NaCl , NaBr , NaI , Na_2S , etc.

(v) Hydrogen possesses strongly reducing properties, typical of strongly electropositive metals (e.g., Na).

(vi) On electrolysis of a hydrogen compound of a non-metal in solution (e.g., HCl), hydrogen ion moves towards the cathode similar to sodium ions in the electrolysis of NaCl solution.



*Concentration of a substance at the surface of another substance, is called adsorption.

Despite the above relationships with alkali metals hydrogen is distinctly a non-metal. Its ability to form negatively charged ions is in direct contrast with alkali metals.

Hydrogen also differs in its ionization energy. It has much higher ionization energy (1321 kJ mol^{-1}) than that of the alkali metals (e.g., $\text{Li}=320 \text{ kJ mol}^{-1}$; $\text{Na}=495 \text{ kJ mol}^{-1}$; $\text{K}=418 \text{ kJ mol}^{-1}$). The extremely small radius of positive hydrogen ion is in marked contrast to the alkali metals, which have the largest radii of all the positive ions in their respective periods (The diameter of H^+ is about 0.00001 \AA ; whereas for all other elements the diameter of the ionic core left after the removal of outermost electron range between 0.2 and 3.3 \AA).

(B) Resemblance with halogens—Electronegative character :

(i) Hydrogen resembles the halogens in having one electron less than the succeeding inert gas in its atom.

Inert gas

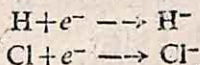
1H	$1s^1$	2He
9F	$1s^2; 2s^2, 2p^5$	10Ne
17Cl	$1s^2; 2s^2, 2p^6; 3s^2, 3p^5$	18Ar
25Br	$1s^2; 2s^2, 2p^6; 3s^2, 3p^6; 4s^2, 4p^5$	36Kr
53I	$1s^2; 2s^2, 2p^6; 3s^2, 3p^6, 3d^{10}; 4s^2, 4p^6, 4d^{10}; 5s^2, 5p^5$	54Xe

(ii) It is a non-metal like the halogens.

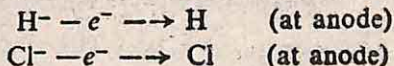
(iii) It forms a diatomic molecule (H:H) by sharing of a pair of electrons between the two hydrogen atoms similar to the halogens (F_2 , Cl_2 , Br_2 , etc.).

(iv) The energy required to dissociate a molecule into its atoms decreases in the sequence H_2 , F_2 , Cl_2 , Br_2 , I_2 .

(v) Hydrogen can gain an electron and form a negative ion, like halogens, e.g.,



With electropositive elements like alkali and alkaline earth metals, hydrogen produces *hydrides which are ionic in character* e.g., Li^+H^- ; $\text{Ca}^{2+}(\text{H}^-)_2$. It was confirmed by Bardwell, in 1922, that when a solution of calcium hydride in a fused mixture of potassium and lithium chloride is electrolysed, hydrogen moves towards the anode just like chloride ions.



(vi) The ionization energy of hydrogen (1321 kJ mol^{-1}) is in close resemblance to the values found for halogens (e.g., $\text{F}=1681 \text{ kJ mol}^{-1}$; $\text{Cl}=1255 \text{ kJ mol}^{-1}$).

(vii) Hydrogen forms covalent compounds like CH_4 , SiH_4 , GeH_4 , AsH_3 with other non-metallic elements just like halogens (e.g., CCl_4 , SiCl_4 and AsCl_3).

On examining the above relationships, it is safe to allow hydrogen to occupy either the top position in group IA or group VIIA in the long form of the periodic table.

1.3. ISOTOPES OF HYDROGEN AND HYDROGEN BOMB

Three isotopes of hydrogen are known. The isotope having only a proton in the nucleus of its atom is 99.985 per cent of the commonly available hydrogen. This is also known as protium and is given the symbol, ${}^1_1\text{H}$. The isotope having a proton and a neutron in the nucleus of its atom has the atomic mass double than that of ordinary hydrogen or protium. This has been given the name *deuterium* and the symbol, D or ${}^2_1\text{H}$. Because of the similarity in their electronic configuration, they show almost similar chemical properties. However, because of the different masses, their physical properties and rates of diffusion are different. For example, ${}^1_1\text{H}$ is adsorbed rapidly on a solid surface than ${}^2_1\text{H}$. Using this difference, they can be separated from each other. *Property difference because of the difference in mass is known as isotopic effect.* Some physical constant are given in Table 1.1 for comparison.

In water deuterium is available upto 0.015% of its hydrogen. Although there is no measurable difference in the chemical properties of the isotopes of any element, deuterium differs significantly in its reactivity from ordinary hydrogen. When water is electrolysed, the electrolysis of ordinary water (H_2O) proceed faster than that of deuterium oxide (D_2O). That is how the concentration of deuterium oxide continuously increases in electrolytic cell used for manufacture of hydrogen and oxygen by electrolysis of water.

There is also a third isotope of hydrogen. The nucleus of its atom possesses one proton and two neutrons. Its atomic mass is three times that of ordinary hydrogen. It is called *tritium* and has been given the symbol ${}^3_1\text{H}$. This occurs in natural hydrogen only

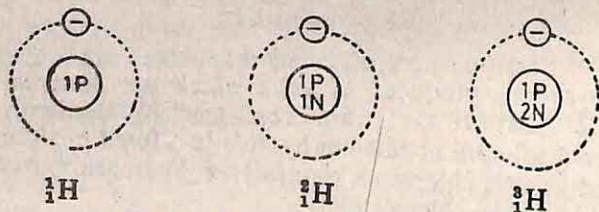
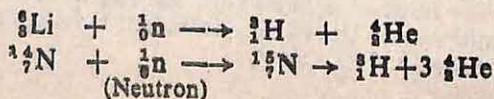


Fig. 1.1. Isotopes of hydrogen.

to the extent of 1 part in 10^9 parts. This isotope is radioactive also. Tritium is produced in nuclear reactions as shown below.

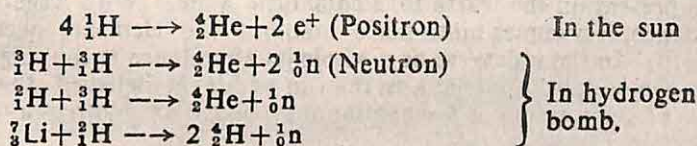


Deuterium and tritium both are also known as *heavy hydrogen*. As tritium is present in a much lesser quantity, so, ordinarily the name heavy hydrogen stands for deuterium. Deuterium oxide is called heavy water (D_2O).

Table 1.1. *Physical properties of hydrogen, deuterium and tritium :*

Property	Protium	Deuterium	Tritium.
Symbol	1_1H	2_1H or D	3_1H or T
Atomic number	1	1	1
Atomic mass	1.008	2.016	3.024
Mass number	1	2	3
Melting point	13.8K	18.5K	—
Boiling point	20.4K	23.9K	—
Latent heat of fusion	117 J mol ⁻¹	219 J mol ⁻¹	—
Latent heat of evaporation	904 J mol ⁻¹	1226 J mol ⁻¹	—
Latent heat of sublimation	1030 J mol ⁻¹	1426 J mol ⁻¹	—
Vapour pressure (at melting point)	54 mm Hg	5.8 mm Hg	—

It is believed that the energy involved in the sun is due to the loss of mass in transformation of hydrogen to helium atoms. In a hydrogen bomb, similar type of reactions seem to occur at very high temperatures.

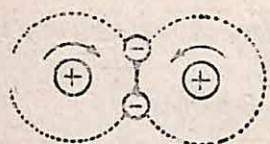


1.4. ORTHO AND PARA HYDROGEN

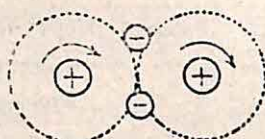
When the two hydrogen atoms combine to produce a molecule the spins of electrons are always in the opposite direction (Pauli exclusion principle). Besides spinning of electrons, the proton present in the nucleus also spins. Thus, in the formation of a hydrogen molecule, the spins of the two protons (or nucleus) may be in the same direction or in opposite directions. *When the spins of the protons are in the same direction, we get ortho hydrogen and when the spins of the protons are in the opposite direction we get para hydrogen* (see Fig. 1.2). These two forms differ slightly in their physical properties. The difference in their thermal conductivities and specific heats, however, are appreciable.

At room temperature (say 298K) ordinary hydrogen is an equilibrium mixture of about 75 percent ortho hydrogen and 25 percent para hydrogen. The proportion of ortho hydrogen, however,

decreases at lower temperature ; while that of para hydrogen increases. At absolute zero, it is almost para hydrogen. Para hydrogen



ANTIPARALLEL SPIN OF
NUCLEI OF HYDROGEN
ATOMS
(PARA HYDROGEN)



PARALLEL SPIN OF NUCLEI
OF HYDROGEN ATOMS
(ORTHO HYDROGEN)

Fig. 1.2

may be prepared by passing normal hydrogen through a tube packed with charcoal cooled to liquid air temperature.

Like hydrogen, deuterium also exists in ortho and para forms. The equilibrium mixture at room temperature consists of 66.7 percent ortho and 33.3 percent para deuterium.

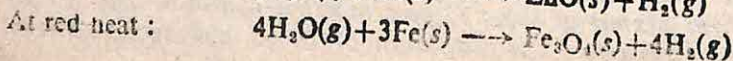
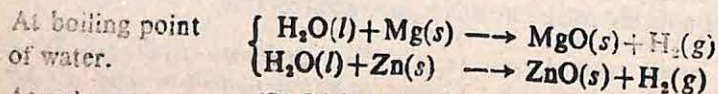
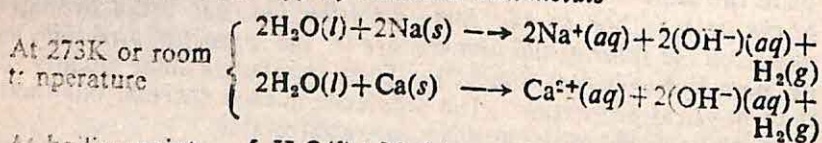
1.5. OCCURENCE AND PREPARATION OF HYDROGEN

In atmosphere the presence of elemental hydrogen is less than one part per 200,000 parts. It is widely distributed in the upper regions of the atmosphere. From there it is slowly disappearing into outer space. In the outer parts of the earth, abundance of hydrogen is only 0.88 percent of the total available hydrogen ; the rest is present on the earth in a combined state. With regard to abundance, it occupies ninth place amongst the elements occurring on earth. In the universe as a whole its abundance is the highest. Hydrogen is most abundant on the sun and it is believed that the source of solar energy is the continuous change of hydrogen nuclei into helium nuclei.

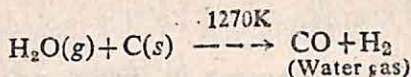
Elemental hydrogen is available in the gases coming out from volcanoes. In combined state it is found in water, acids, alkalies, hydrocarbons and it is an important constituent of almost all organic compounds.

Preparation of hydrogen. Hydrogen can be prepared by one of the following methods :

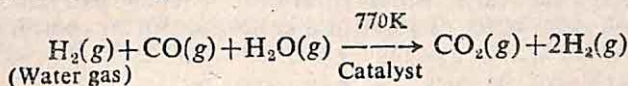
(1) From water. (i) By reactions with metals



(ii) *By action of steam on red hot coke.*



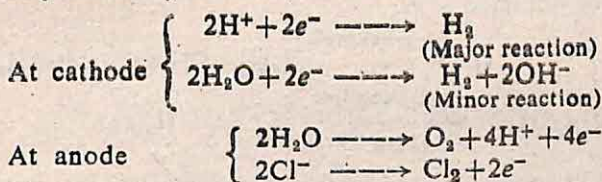
It is difficult to separate CO from H₂ and, therefore, CO is oxidised to CO₂ in the following way.



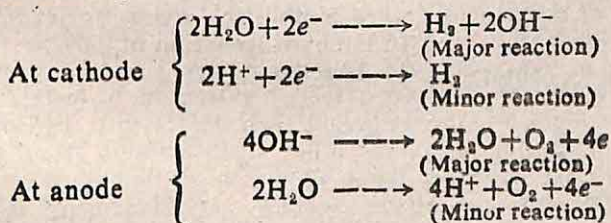
Hydrogen is then separated by dissolving CO₂ in cold water under pressure.

(iii) *By electrolysis.* For this water has to be made electrically conducting. This can be done by adding to it small quantity of an acid or alkali. When electricity is passed, hydrogen is liberated at cathode and oxygen or some other substance is liberated at the anode. The electrochemical reactions are given below :

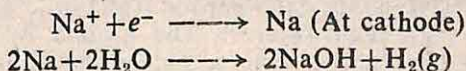
In presence of an acid (like HCl).



In presence of an alkali. In alkali solutions the concentration of H⁺ ions becomes negligible and we have a high concentration of OH⁻ ions. The reactions occurring at the electrodes under these conditions are :

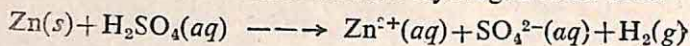


Although in alkaline solutions there is a high concentration of alkali metal ions (like Na⁺) yet in the presence of water the acceptance of electrons by Na⁺ ions do not occur as this reaction is highly endothermic and thus needs a much higher electrodes potential. However, before that is reached the electrolysis of water starts. The following reactions are found in number of books, these should be avoided.



Note. Formation of sodium metal by electrolysis in presence of water is not possible except when mercury is used as cathode.

(2) *From acid.* A few metals liberate hydrogen from acid.

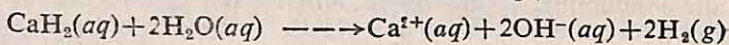


or in general : $\text{M}(s) + n\text{H}^+(aq) \longrightarrow \text{M}^{n+}(aq) + \frac{n}{2} \text{H}_2(g)$

(3) *From alkalis.* Very few metals can displace hydrogen from strong alkalis and their water solutions. Metals like zinc, aluminium, which can do so, dissolve in alkalis to form complex anions, e.g.,

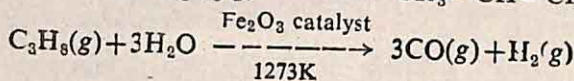
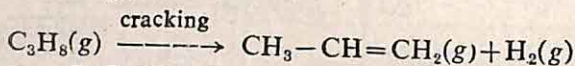


(4) *From metal hydrides and hydrocarbons.* The metal hydrides also yield hydrogen when treated with water e.g.,



The commercial name for calcium hydride is "hydrolith".

Natural gas, hydrocarbons and oils are important materials for obtaining hydrogen. By their cracking or fractional oxidation hydrogen may be obtained. e.g.,



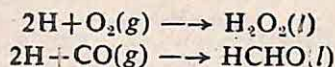
Crude oil or naphtha is used by fertilizer factories for producing hydrogen for making ammonia.

Uses of hydrogen. (i) In the manufacture of ammonia and artificial fertilizers based on it. (ii) In the manufacture of methyl alcohol and formaldehyde from carbon monoxide. (iii) As a fuel gas alone or mixed with other combustible gases (for example, water gas and coal gas). (iv) In the hydrogenation of oils to form solid fats (sold as vanaspati). (v) As reducing agent and for producing atmosphere free from oxygen. (vi) In extraction of metals like tungsten and molybdenum by reducing their oxides with hydrogen. (vii) For manufacturing petrol and other hydrocarbons from hard coke. (viii) In oxy-hydrogen flame used for welding purposes (to produce a temperature of about 3000K). (ix) Hydrogen is the lightest known gas and is used for filling experimental balloons. A mixture of 85% He and 15% H_2 is non-combustible and is used for filling aeroplane tyres. (x) As a cooling gas for hot substances.

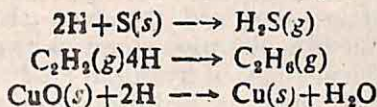
1.6. ATOMIC HYDROGEN

The change $\text{H}_2 \longrightarrow 2\text{H}$, involves the absorption of 433 kJ mol^{-1} of heat, i.e., the conversion of molecular hydrogen to atomic hydrogen is an endothermic reaction. The dissociation is favoured at high temperatures. The atomic hydrogen thus produced is highly reactive and combines almost instantaneously to produce molecules of hydrogen releasing the same amount of energy as absorbed by molecular hydrogen for its dissociation. The

reaction is catalysed in presence of metals. Atomic hydrogen is highly reactive and combines with oxygen to form peroxide and with carbon monoxide to form formaldehyde.



It combines easily with sulphur, phosphorus, sodium, potassium, etc., forming their respective hydrides. It also reduces unsaturated hydrocarbons to saturated ones and cupric oxide into metal.



The life period of atomic hydrogen is only 0.03 second. However, some believe that it can be extended to 10 seconds.

Atomic hydrogen is generally produced by blowing a jet of molecular hydrogen through an electric arc struck between tungsten

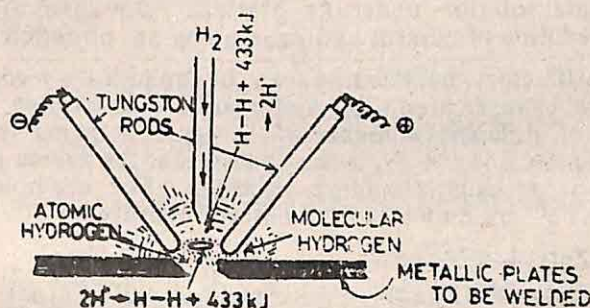
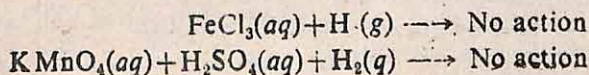


Fig. 1.3. Atomic hydrogen torch

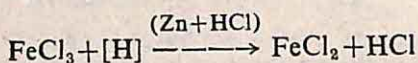
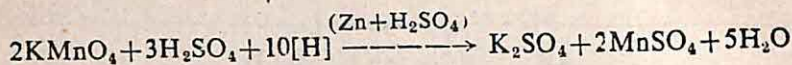
electrodes. This is how atomic hydrogen is produced in *hydrogen welding torch* (Fig. 1.3). Atomic hydrogen issuing from the arc strikes the metallic surface, which acts as a catalyst, when the atoms recombine into molecular hydrogen with the liberation of heat ($2\text{H} \longrightarrow \text{H}_2 + 433 \text{ kJ}$). The liberated heat raises the temperature of the metal to 4200–5200K.

1.7. NASCENT HYDROGEN

Hydrogen formed in a reaction is initially very reactive. This *hydrogen at the moment of its birth is known as nascent hydrogen*. If the newly born hydrogen can be directly used, in some reaction, it proves to be highly reactive. For example, when hydrogen gas is passed through a solution of ferric chloride or potassium permanganate, no change takes place.



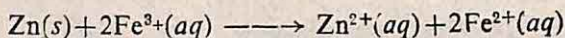
If however, we put a piece of zinc in an acidified solution of potassium permanganate or ferric chloride reduction takes place, as indicated by the disappearance of colour.



Earlier it was believed that hydrogen at the moment of its liberation exists in atomic stage and therefore, showed exceptional activity. But this simple explanation seems to be untenable in view of varying power of reduction of hydrogen produced from different sources. For example, nascent hydrogen produced by sodium-amalgam does not reduce potassium chlorate but it reduces nitrates to hydronitrites.

Another explanation given is that tiny bubbles produced in reaction are under great pressure and hydrogen gas under high pressure will have greater reactivity. So, it precipitates silver from silver nitrate solution under its pressure. But again the varying power of reduction of nascent hydrogen poses an objection to it.

A satisfactory explanation can be found if we recognise that the chemical changes producing hydrogen are associated with the liberation of different amounts of energy. Thinking in terms of electron transfer and energy, it can be said that the source producing hydrogen is actually providing electrons. For example Fe^{3+} is reduced to Fe^{2+} by Zn and not by nascent hydrogen.

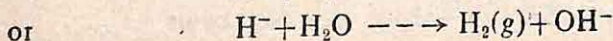
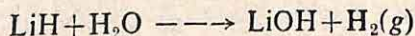


1.8. HYDRIDES

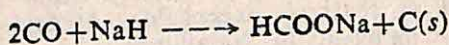
Binary compounds of hydrogen and other elements are called hydrides. Depending on the electronegativities of the elements, following types of hydrides are formed.

(1) **Ionic hydrides.** These hydrides are formed by hydrogen with elements having low electronegativities. For example, the elements belonging to group IA and IIA (leaving Be and Mg) form these hydrides. f-block elements also produce ionic hydrides.

These are crystalline solids having salt-like lattices. Their melting points are high. Except lithium hydride, all decompose on fusion. Electrolysis of fused LiH (or some other hydride dissolved in suitable melt) produces hydrogen at the anode showing the presence of hydride ion, H^- (see section 1.1). They are hydrolysed vigorously by water with the formation of corresponding hydroxide and hydrogen, e.g.,



They are powerful reducing agents specially at higher temperature, e.g.,

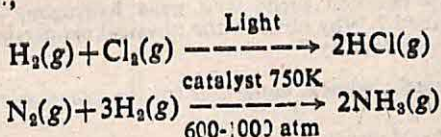


LiH and NaH are used in making valuable reducing agents LiAlH_4 (lithium aluminium hydride) and NaBH_4 (sodium borohydride).

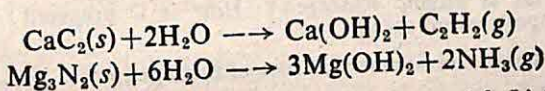
(2) **Molecular or covalent hydrides.** *These are formed by most p-block elements, which have comparatively high electronegativity value. The stability of a covalent hydride within a group decreases as atomic number increases. However, the stability of hydrides increases with the increase of electronegativity (i.e., when we move from left to right in any period of the periodic table). They are mostly gaseous compounds in which the elements exhibit their group valencies.*

The covalent hydride may be prepared by the following methods.

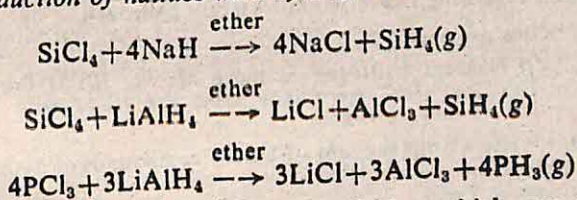
(i) *By direct combination of the elements under suitable condition, e.g.,*



(ii) *By the hydrolysis of carbides, nitrides and phosphides, e.g.,*



(iii) *Reduction of halides with hydrogen or with LiAlH_4 .*



Elements of group IIIA form hydrides which are electron deficient and polymeric. The most important and simplest hydride of boron is B_2H_6 (diboron). Beryllium, magnesium and aluminium also form hydrides having the composition $(\text{BeH}_2)_n$, $(\text{MgH}_2)_n$ and $(\text{AlH}_3)_n$, which are polymeric and are known as polynuclear hydrides.

(3) **Metallic hydrides or interstitial hydrides.** *These are formed by some transition metals (d block elements) with electronegativities ranging from 1.2 to 1.4. They are non-stoichiometric solids like $\text{PdH}_{0.6}$, $\text{TiH}_{1.73}$, $\text{ZrH}_{1.98}$, in which hydrogen occupies interstitial positions in the metal lattice. Proportion of hydrogen in the compound depends upon the temperature and pressure*

They may be prepared by heating the metal in hydrogen (under varying pressure) or by electrodeposition of hydrogen on the metal used as (cathode except Pd). Hydrides of Ti and Zr are used as reducing agents in metallurgy.

f-block elements also form hydrides of non-stoichiometric composition such as $\text{LaH}_{2.78}$; $\text{CeH}_{2.69}$ and $\text{ThH}_{3.07}$ close to those of group IA and group IIA metals. Hence, they are classed as having intermediate character between ionic and metallic hydrides.

QUESTIONS

(A) Essay Type

1. Discuss the unique position of hydrogen in the periodic table.
2. How does hydrogen resemble alkali metals? Also discuss the similarities of hydrogen with halogens.
3. Name the isotopes of hydrogen. How do they differ from one another? What principle is used in the separation of these isotopes?
4. Differentiate between ortho and para hydrogen. How can pure para hydrogen be obtained? Why most of the physical properties of ortho and para hydrogen differ considerably?
5. Write balanced chemical equations for the preparation of hydrogen from the following :

(a) a metal and water,	(b) a non-metal and water,
(c) a metal and an acid,	(d) a metal hydride and water.
6. What is atomic hydrogen? How is it prepared? What are its important properties and uses?
7. Describe the commercial uses of hydrogen.
8. What is nascent hydrogen? How is it prepared? Give different explanations regarding the activity of nascent hydrogen.
9. Give reasons.

(i) Nascent hydrogen is more active. (ii) Hydrogen is filled in balloons. (iii) Aeroplane tyres are filled with a mixture of helium and hydrogen.
10. Write a brief account of binary compounds of hydrogen.

(B) Short Answer Type

11. How can hydrogen be separated from water gas?
12. What is the ratio of ortho to para hydrogen at room temperature? How can pure para hydrogen be obtained?
13. What is the commercial name for calcium hydride? How is hydrogen prepared from it?
14. Give the principle underlying 'atomic hydrogen torch' used in metal welding.
15. What are ionic hydrides? Why are they so-called?
16. What are metallic hydrides? Give two examples of these compounds and their uses.

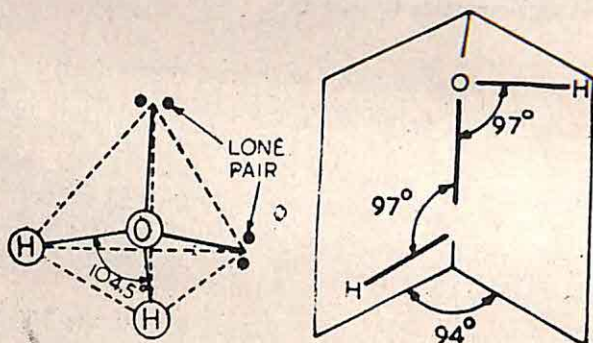
(C) Objective Type

17. Put a tick mark for the correct answer :

- (a) Which one of the following metals does not produce hydrogen with water ? (i) lithium, (ii) sodium, (iii) calcium, (iv) palladium.
- (b) Hydrogen burn with a (i) smoky flame, (ii) luminous flame (iii) pale blue flame, (iv) pale green flame.
- (c) The commercial name for calcium hydride is (i) caustic potash, (ii) hydrolyth, (iii) slaked lime, (iv) carbogas.
- (d) Hydrogen is a reducing agent but it can not reduce (i) cupric oxide to copper, (ii) ferric oxide to iron, (iii) tungsten oxide to tungsten, (iv) calcium oxide to calcium.

☐ ☐ ☐

Water and Hydrogen Peroxide



2.1. PHYSICAL PROPERTIES OF ORDINARY WATER

- | | |
|---|--------------------------------|
| (1) Molecular formula | = H_2O |
| (2) Melting Point | = 273K |
| (3) Boiling Point (at one atmospheric pressure) | = 373K |
| (4) Critical temperature | = 673K |
| (5) Critical pressure | = 517.7 atmospheres. |
| (6) Critical volume | = 56.6 ml mol ⁻¹ |
| (7) Density at 277 K | = 1.0 g cm ⁻³ |
| (8) Molecular mass | = 18.015 |
| (9) Vapour pressure | = 17.4 ml at 293K |
| (10) Latent heat of fusion at 273K | = 6 kJ mol ⁻¹ |
| (11) Latent heat of vaporisation at 373K | = 40.6 kJ mol ⁻¹ |
| (12) Specific heat at 288K | = 1.00 cal. g ⁻¹ |
| (13) Coefficient of volume expansion at 293K | = 2.07×10 per degree. |
| (14) Dielectric constant (at 293K) | = 82.0 |

Pure water is a colourless, odourless, tasteless and transparent liquid. Its very light blue colour deepens with depth of layer; open seas have a beautiful blue colour. It is a poor conductor of heat and electricity. At 277 K water possesses its maximum density of 1.0 g cm^{-3} . At temperatures above and below 277 K, water expands and its density decreases as shown in Table 2.1. The specific heat of water is practically the highest.

Table 2.1. Effect of temperature on density of water.

Temperature (K)	Density (g cm^{-3})	Temperature (K)	density (g cm^{-3})
272 ice	0.917	277	1.0
273 water (l)	0.99987	278	0.99999
274	0.99993	279	0.99997
275	0.99997	283	0.99973
276	0.99999	293	0.99823

Its physical constants are taken as reference values for determining similar constants for other substances.

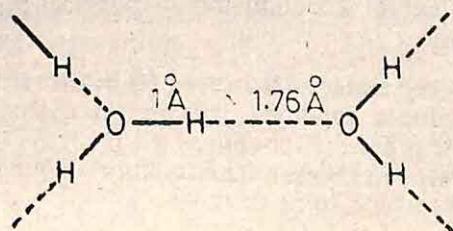
When water at 273 K changes to ice there is an expansion. Hence, we notice that ice floats on liquid water.

2.2. GENERAL DESCRIPTION

Water is the most abundant and widely distributed substance on earth. It occurs in all its three physical forms viz., solid, liquid and gaseous. Ice and snow are its solid forms. Liquid water covers almost three quarter of earth's surface, and as water vapour it is present in the atmosphere. Water is present in all living matter and most foods. It comprises almost 65% of the human body.

2.3. STRUCTURE OF WATER MOLECULES

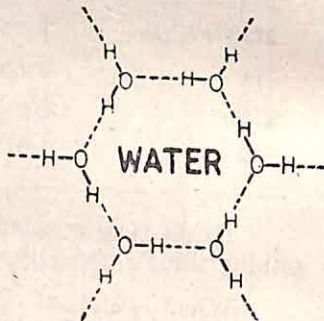
The water molecule has an angular shape with a bond angle of 104.5° . The O—H bond length is 1.0 \AA . Since oxygen is highly electronegative compared to hydrogen, water molecule is highly polar. The oxygen atom becomes the negative pole and the positive pole is located centrally between the two hydrogen atom. Due to the polar structure of molecules, an attractive force operates between



neighbouring water molecule and hence a special situation is established in liquid water. In such a situation, the oxygen atom of one water molecule attracts the hydrogen atom of a neighbouring molecule, pulling it to an equilibrium distance of 1.76 \AA . Thus, the distance between the oxygen atoms of neighbouring water molecules becomes $1 + 1.76$ or 2.76 \AA . The weak chemical bond formed between the two electronegative atoms by having a proton in between is known as hydrogen bond. It may be shown by a dotted lines to distinguish it from normal bonds. The $\text{O-H} \cdots \text{O}$ bond angle is 180° . When such a situation is possible, the hydrogen bond bridges will link up a large and undefined number of molecules.

Due to the formation of hydrogen bonds in water, its properties are different from those of the hydrogen compounds of other elements such as H_2S and H_2Se . In particular, the melting and boiling points of water are comparatively much higher than those of comparable other compounds.

When water crystallises to form ice interlinking tetrahedrons are formed by the hydrogen and oxygen atoms. Such structure has relatively more of vacant space. Due to empty spaces in the solid form, density of ice is less than that of water and we find that ice floats on water. When ice melts some tetrahedral structures continue to exist and the complete breakdown is reached at 277 K . Due to this, density of water increases from 273 K . Structure of ice is shown in Chapter 4 of part I.



2.4. HEAVY WATER

The credit for the discovery of heavy water goes to Urey, an American chemist. He showed that ordinary water contains one part of heavy water in 6000 parts. Lewis and Denials, in 1933, were able to prepare a few milli-litres of practically pure heavy water by long, continued electrolysis of water containing alkali. It has already been said in section 1.2 that concentration of heavy water (D_2O) goes on increasing in the cell used for preparing oxygen or hydrogen by electrolysis (since the electrolysis of D_2O is slow compared to H_2O). This method is used for manufacturing heavy water. Like ordinary water, D_2O is a colourless, odourless and testless liquid. Table 2.2 compares its physical property with those of ordinary water.

Uses of heavy water. It is used (i) in the study of exchange reactions by isotopic methods, (ii) in the preparation of heavy hydrogen and its other compounds, e.g., DCl , ND_3 , $\text{C}_2\text{H}_5\text{OD}$, etc. (iii) as a moderator in nuclear reactions for slowing down the fast neutrons and absorbing some of them.

In India, we manufacture D_2O for our needs at Bhabha Atomic Research Centre, Bombay.

Table 2.2. *Physical constants of H₂O and D₂O*

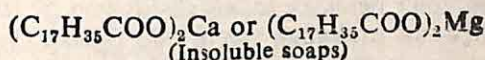
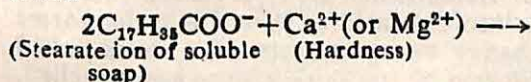
<i>Physical Property</i>	<i>Ordinary Water (H₂O)</i>	<i>Heavy Water (D₂O)</i>
Melting point	273K	276.8
Boiling point	373K	374.42K
Temp. of maximum density	277K	284.4K
Ionic product	1.0×10^{-14}	1.0×10^{-15}
Critical temp.	647K	644K
Surface tension at 293K	72.5×10^{-3} newton m ⁻¹	67.8×10^{-3} newton m ⁻¹
Dielectric constant at 293K	82	80.5
Solubility (g NaCl/100g water) at 298K	35.9	30.5

Uses of heavy water. It is used (i) in the study of exchange reactions by isotopic methods, (ii) in the preparation of heavy hydrogen and its other compounds, e.g., DCl, ND₃, C₂H₅OD, etc., (iii) as a moderator in nuclear reactions for slowing down the fast neutrons and absorbing some of them.

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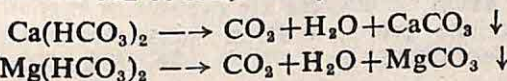
2.5. SOFT AND HARD WATER

Water which easily forms lather with soap is known as soft water, and water which does not easily form lather with soap (instead forms curdy precipitate of insoluble soap) is known as hard water. The hardness of water is due to the presence of soluble salts of calcium and magnesium such as bicarbonates, chlorides and sulphates. The presence of sodium and potassium salts does not make water hard. Calcium and magnesium ions react with ordinary soap (like sodium stearate) to form insoluble soaps of higher fatty acids.



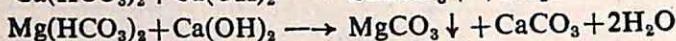
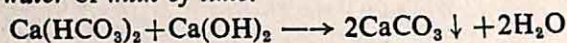
Hardness of water is of two kinds. Temporary hardness is due to the presence of bicarbonates of calcium and magnesium; and the permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium.

Temporary hardness can be removed by mere boiling :



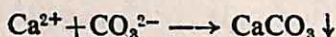
Carbonates of calcium and magnesium are insoluble and can be removed by filtration or decantation. Temporary hardness can

also be removed by addition of requisite quantity of lime in the form of *lime water* or *milk of lime*.

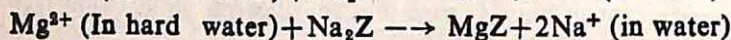
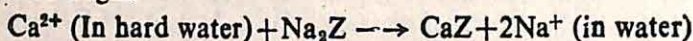


Permanent hardness can be removed by any of the following methods :

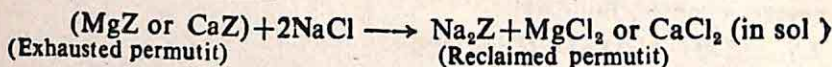
(i) *By precipitation.* Calcium or magnesium salts (usually chlorides and sulphates) are precipitated by addition of Na_2CO_3 , Na_3PO_4 or NaOH . The precipitate may be filtered or decanted, e.g.,



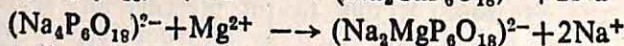
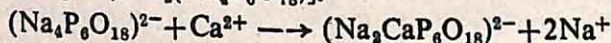
(ii) *Permutit Process.* By passing hard water through a bed of artificial zeolites (complex sodium aluminosilicates $\text{Na}_2\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$, abbreviated as Na_2Z ; and known as permutit). Calcium and magnesium ions present in hard water are changed to insoluble CaZ or MgZ .



Exhausted permutit may be regenerated by passing 10% sodium chloride solution.



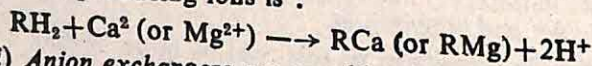
(iii) *Calgon Process.* By passing hard water through a bed of Calgon [complex, $\text{Na}_2(\text{Na}_4\text{P}_6\text{O}_{18})$].



Thus, the Ca^{2+} and Mg^{2+} ions remain in solution as a part of the complex anion and the presence of these in this form does not interfere in the use of water.

(iv) *Demineralization or Deionization process.* As ion exchange resin may be regarded as an insoluble acid or base which also forms insoluble salts. An ion exchange resin consists of a cross-linked polymer network to which ionized or ionizable groups are attached. The ion exchange are of two types :

(i) *Hydrogen or cation exchangers.* The main functional groups in cation exchange resins are $-\text{SO}_3\text{H}$, $-\text{COOH}$, etc. Hydrogen exchangers are generally represented as RH_2 . So, their reaction with hardness producing ions is :

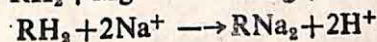


(ii) *Anion exchangers* are capable of exchanging anions. The main functional groups in anion exchangers are $-\text{OH}$, and $-\text{NH}_2$. They are represented as $\text{R}'(\text{OH})_2$. So, their exchange reactions with anions are :



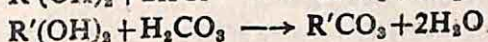
From above it is clear that if hard water is passed first through cation exchanger bed and then through anion exchanger bed, the resulting water will be free from both cations and anions, i.e., deionized or demineralized because the H^+ ions produced by cation exchanger reacts with OH^- produced by anion exchanger forming water. Consequently, the use of ion exchange resins produces virtually distilled water.

Demineralization process consists in passing hard water first through cation exchanger bed Fig. 2.1, which removes all the cations like Ca^{2+} , Mg^{2+} , Na^+ , etc., and release hydrogen ions.



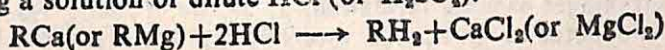
Thus, sulphates, chlorides and bicarbonates are converted into corresponding acids, H_2SO_4 , HCl and H_2CO_3 respectively.

After this water is passed through an anion exchanger bed where acids are converted into water.



Consequently, water thus produced is free from all ions.

When cation resins get exhausted (i.e., when their capacity to exchange respectively H^+ or OH^- is lost) they are regenerated by passing a solution of dilute HCl (or H_2SO_4).



The washing containing $CaCl_2$, $MgCl_2$, etc., (or $MgSO_4$, $CaSO_4$) is passed to a sink.

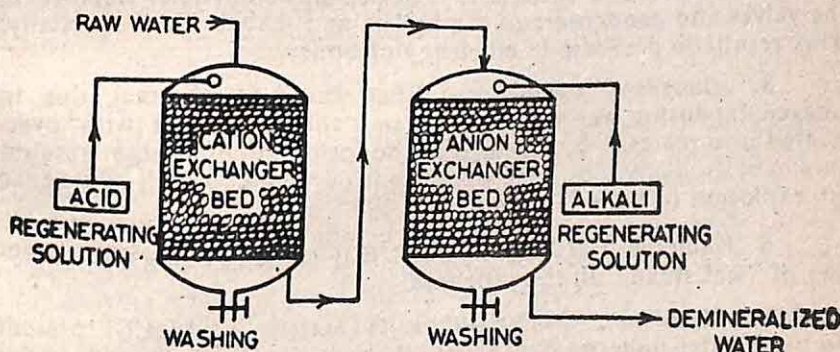
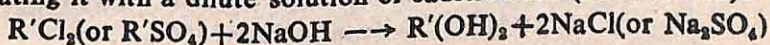


Fig. 2.1. Demineralization of water.

Similarly, the exhausted anion exchanger is regenerated by treating it with a dilute solution of caustic soda (or soda ash).

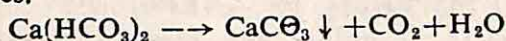


The washings containing NaCl , Na_2SO_4 , etc., are also led to a sink.

2.6. TREATMENT OF WATER FOR INDUSTRIAL PURPOSES

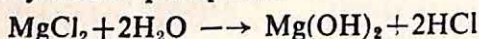
Water in industries is mainly used in boilers for raising steam. In boiler, water evaporates continuously and the concentration of the dissolved salts increases. After some time the dissolved salts are thrown out (or precipitated) of water and get desposited as hard crusts on the inner walls of the boiler. They are called as scales. The formation of scales are due to :

(i) *Decomposition of bicarbonates.* Calcium and magnesium bicarbonates present in hard water decompose in boiler forming insoluble carbonates.



(ii) *Deposits of calcium sulphate.* The solubility of this salt in water decreases with rise of temperature. So, on heating hard water in boiler, calcium sulphate gets precipitated.

(iii) *Hydrolysis of magnesium salts.* Dissolved magnesium salts undergo hydrolysis at high temperature inside the boiler, forming magnesium hydroxide precipitate.



(iv) *Presence of silica.* Silica even present in small quantities, deposits as calcium or magnesium silicate. This deposit sticks very firmly on the boiler plates and is very difficult to be removed.

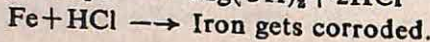
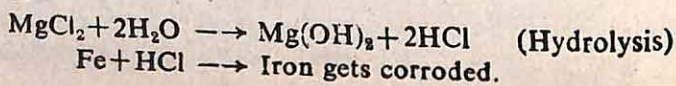
Disadvantages of scale formation. 1. *Waste of fuel.* As scales are poor conductor of heat, the rate of heat transfer from boiler to water is greatly decreased. So, excessive heating is to be done. Thus, a larger quantity of fuel is consumed.

2. *Decrease in efficiency.* Scales may sometimes deposit in the valves and condensers of the boiler and chock them partially. This results in decrease in efficiency of boiler.

3. *Danger of explosion.* When thick scales crack due to uneven expansion, the water comes suddenly in contact with overheated iron plates. This causes in the formation of a large amount of steam suddenly. So, huge pressure is developed, which may cause an explosion of boiler.

4. *Foaming.* Hardness in water may cause foaming and carrying of "wet steam" in the pipelines.

5. *Corrosion.* Magnesium salts (particularly MgCl_2) present in hard water undergo hydrolysis at high temperature and under high pressure inside the boiler. On hydrolysis HCl is produced which attacks the boiler material (i.e., iron) and shortens its life due to corrosion.



Hence, water used for raising steam in boilers should be free from soluble as well as suspended impurities.

2.7. DRINKING WATER

Drinking water should be colourless, odourless, clear, tasty, free from injurious dissolved and suspended impurities and should be absolutely free from pathogenic bacteria and germs.

When the drinking water is not sufficiently pure, purification becomes necessary. A number of methods are used for purification. Main aim in each case is to remove suspended impurities and to destroy pathogenic bacteria.

(i) **Methods of removing suspended impurities.** (i) Water from a natural source if turbid, is made to stand for some time in large tanks. It helps in killing bacteria through the effects of dissolved air and sunlight. The suspended impurities, sand, clay, etc., settle down and clear water is separated by decantation. This may be further purified according to needs.

(ii) If the suspended impurities are present in colloidal state, they may be coagulated by adding common alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$.

(iii) On a large-scale suspended impurities are removed by filtration. The impure water is led to the filter beds of sand and gravel (Fig. 2.2) which holds back the suspended impurities as well as most of bacteria. The filtered water is collected from below.

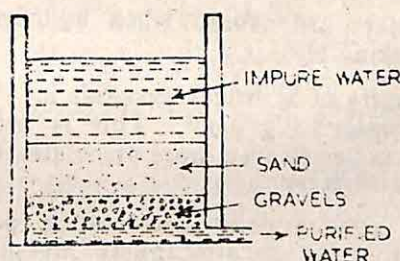


Fig. 2.2. Filtration on large scale.

After a few weeks filter beds may get clogged. The filtration is stopped and top layer of sand is scrapped off and fresh layer of sand is refilled and beds is used again.

(2) **Methods for killing bacteria and germs.** The process of killing disease carrying germs or bacteria is known as *sterilization*. Following methods are in use for this purpose.

(i) **Boiling.** All kinds of bacteria are destroyed by boiling. This method can be used only in homes when small quantities of safe drinking water are to be made in days of epidemics.

(ii) **Chlorination.** Chlorine is an excellent germicidal gas and hence chlorine in the form of liquid chlorine or bleaching powder is mixed with water to kill germs. Chlorine should not be used in

excess. The quantity of free chlorine present in water should not be more than 0.25 parts per 1,000,000 parts of water. Excess of chlorine may be removed later on by passing ozonised oxygen and adding a small amount of ammonia. This also improves the, otherwise, unpleasant taste of chlorinated water.

(iii) *Ozonisation.* Ozone is also a strong disinfectant. When ozone is passed in water it kills germs.

(iv) *By ultraviolet rays.* These rays are used for quick sterilization. They are obtained from mercury vapour lamp. Mercury vapour lamps are fitted under water in swimming pools to keep the water free from disease communicating germs.

(v) *Oxidation by aeration.* In this method water is sprayed into air. Oxygen of air and active rays of sunlight destroy bacteria and organic matter. This method is largely used in America.

Water supplies of big cities are sterilized by above mentioned methods.

2.8. PROPERTIES OF HYDROGEN PEROXIDE, H_2O_2

Physical. (i) Pure anhydrous hydrogen peroxide is colourless syrupy liquid.

(ii) It has a bitter taste when tasted after dilution.

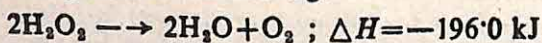
(iii) It mixes with water in all proportions. Besides this, it is soluble in alcohol and ether in all proportions.

(iv) Blisters are caused when hydrogen peroxide comes in contact with skin.

(v) Density of hydrogen peroxide is 1.44 g cm^{-3} at 272K as compared to water 1.0 g cm^{-3} . This is because the molecules of hydrogen peroxide are even more associated by hydrogen bond than the molecules of water.

(vi) Its melting point and boiling point are 272.14K and 23K respectively at one atmospheric pressure. As it decomposes vigorously above 413K ; its boiling point has been determined by extrapolation.

Chemical. (i) *Decomposition.* Hydrogen peroxide is an unstable compound which decomposes, into water and oxygen on keeping for a long time or on heating.

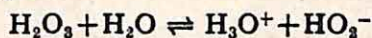


The rate of decomposition of hydrogen peroxide increases in presence of alkalies, or solid particles e.g., dust, carbon, metal powders, MnO_2 , organic tissues, rough surface and light. Therefore, it is kept in waxlined (smooth) brown bottles to save it from decomposition.

Its dilute solution may be kept almost stable by the presence of a small amount of a stabilizer, e.g., acetanilide, alcohol, phos-

phoric acid and glycerol, etc. These act as a "negative catalyst" to the decomposition of hydrogen peroxide.

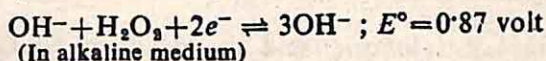
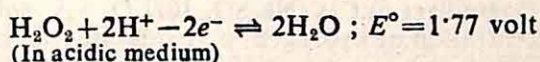
(ii) *Acidic nature.* The aqueous solution of hydrogen peroxide is very weakly acidic.



It gives two series of salts, peroxides and hydroperoxide, e.g., Na_2O_2 and NaHO_2 . They yield hydrogen peroxide on acidification, e.g.,

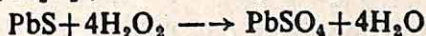
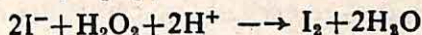
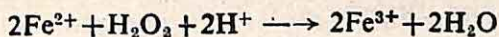


(iii) *Oxidising properties.* Hydrogen peroxide is a powerful oxidising agent in acidic and alkaline medium. Like all other oxidising agents it functions as an *electron acceptor*.

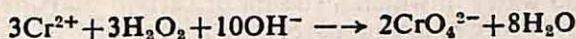


The electrons are supplied by the reducing agent present. Oxidation is generally slow in acidic medium, but rapid in alkaline medium.

Some important examples of oxidation of hydrogen peroxide in *acidic medium* are :



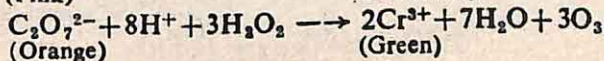
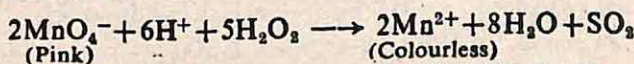
Some important examples of oxidation of hydrogen peroxide in *alkaline medium* are :



Due to its oxidising property, it is a valuable bleaching agent, powerful but harmless disinfectant and germicide. Delicate material like silk, wool, hair, (which are destroyed by chlorine) are bleached with hydrogen peroxide.

(iv) *Reducing properties.* Hydrogen peroxide also acts as a reducing agent (*electron donor*) towards several substances, which themselves are powerful oxidising agents. It can act as reducing agent in acidic as well as in alkaline medium.

In "acidic medium" it decolourless acidified permanganate or acidified dichromate :

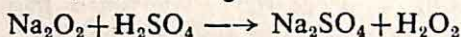


In "alkaline medium" it reduces ferricyanide to ferrocyanide :
 $2(\text{Fe}(\text{CN})_6)^{3-} + 2\text{OH}^- + \text{H}_2\text{O}_2 \longrightarrow 2(\text{Fe}(\text{CN})_6)^{4-} + 2\text{H}_2\text{O} + \text{O}_3$

2.9. METHODS OF PREPARATION OF HYDROGEN PEROXIDE

While preparing hydrogen peroxide the temperature should be kept low and the solution should not be alkaline, as otherwise the hydrogen peroxide formed will decompose.

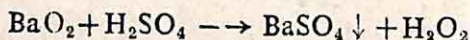
(i) **By the action of dilute sulphuric acid on sodium peroxide.** Sodium peroxide is added in small amounts to ice cold 20% dilute sulphuric acid with constant stirring.



On cooling the solution with freezing mixture, most of sodium sulphate crystallizes out as $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. A solution of about 30% concentration of hydrogen peroxide is left behind as mother liquor.

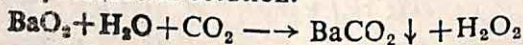
Note. If sulphuric acid is added to Na_2O_2 then solution being alkaline in the beginning, the hydrogen peroxide formed will decompose.

(ii) **By the action of dilute sulphuric acid on barium peroxide.** In this method barium peroxide is made into a paste with cold water and then added in small amounts to ice cold dilute sulphuric acid with constant stirring.

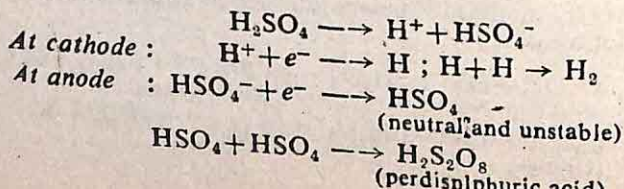


The precipitate of barium sulphate settles down. On filtration a dilute solution of hydrogen peroxide is obtained.

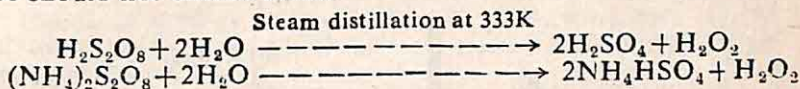
(iii) **Merk's process.** The barium peroxide paste is gradually added to cold water in which a stream of carbon dioxide is bubbling. The less soluble barium carbonate is precipitated out leaving behind hydrogen peroxide in solution.



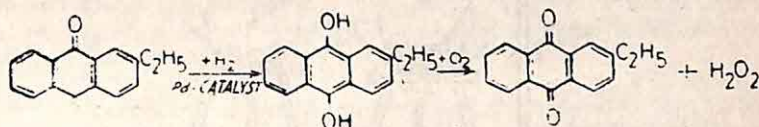
(iv) **Electrolytic process.** This is the modern method for preparing hydrogen peroxide on a large scale. A 50% solution of sulphuric acid maintained at 283K is electrolysed and the product obtained at the anode is hydrolysed or distilled in vacuum. The anode and cathode are made of platinum and graphite respectively and are kept separated by using a porous silica diaphragm. A 30% solution of hydrogen peroxide is obtained. The presence of a small amount of ammonium bisulphate increases the yield. The following reactions take place :



The perdisulphuric acid obtained at the anode or its ammonium salt is subjected to steam or vacuum distillation. The temperature should not exceed 333K.



(v) **Auto-oxidation method.** This is the most modern method of manufacture hydrogen peroxide. In this a derivative of anthraquinone (ethyl anthraquinone) is reduced to anthraquinol (ethyl



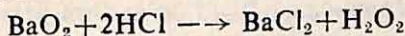
anthraquinol) by dissolving it in an organic solvent and passing hydrogen through it in the presence of palladium (catalyst). On bubbling air through the anthraquinone derivative, a 20% solution of hydrogen peroxide is obtained and anthraquinone derivative is regenerated.

H_2O_2 produced is extracted with water from the carbon solvent and is concentrated.

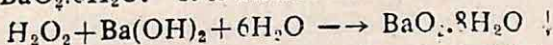
2.10. PREPARATION OF HYDROGEN PEROXIDE IN THE LABORATORY

In the laboratory it is prepared by the action of ice cold dilute sulphuric acid and hydrated crystalline barium peroxide ($\text{BaO}_2 \cdot 8\text{H}_2\text{O}$). If hydrogen peroxide is prepared by the action of cold dilute sulphuric acid on anhydrous barium peroxide then the barium sulphate formed is deposited on barium peroxide particles and the formation of hydrogen peroxide stops. When hydrated crystalline barium sulphate is taken for the purpose, sealing of particles does not happen.

To prepare hydrated barium peroxide ($\text{BaO}_2 \cdot 8\text{H}_2\text{O}$) the powder of anhydrous BaO_2 is treated with 50% hydrochloric acid solution till the solution becomes neutral.



Then, to it a saturated solution of barium hydroxide is added to precipitate $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$. It is filtered and washed.



When this hydrated crystalline barium peroxide is treated with ice cold dilute sulphuric acid, barium sulphate is precipitated and hydrogen peroxide is left in solution.



2.11. CONCENTRATION OF HYDROGEN PEROXIDE SOLUTION

Hydrogen peroxide solutions obtained by the above methods are of about 20 to 30% concentration and generally hydrogen peroxide of the same concentration is used for different purposes.

If necessary it can be made more concentrated by the following steps :

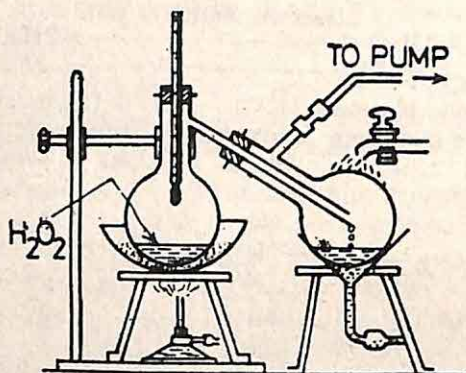


Fig. 2.3. Distillation of hydrogen peroxide under reduced pressure.

(i) A solution of about 65% concentration may be obtained without appreciable decomposition, by evaporating dilute solution on water bath maintained at 333 to 343K.

(ii) 65% solution of hydrogen peroxide obtained by evaporation may be concentrated upto 90% by distilling it under reduced pressure (65 mm) between 333 to 343K.

(iii) 90% solution of hydrogen peroxide may be concentrated upto 99% by keeping it in a vacuum desiccator.

To remove the last traces of hydrogen peroxide, the 99% solutions is kept in a freezing mixture of solid carbon dioxide and ether and thus the crystalline hydrogen peroxide is formed. By warming these crystals hydrogen peroxide of 100% concentration is obtained. The crystals formed, however, are highly explosive.

2.12. TESTS OF HYDROGEN PEROXIDE

(i) It decolourises acidified potassium permanganate.

(ii) It develops a blue colour with acidified potassium dichromate. On shaking it with ether, the colour of the ether layer turns deep blue.

(iii) It liberates iodine from potassium iodide in presence of ferrous sulphate.

2.13. USES OF HYDROGEN PEROXIDE

(i) It is a non-poisonous antiseptic and a dilute solution is widely used for washing wounds, teeth, ear, nose, etc., under the name *perhydrol*. (ii) It is also a mild bleaching agent and is used to bleach delicate materials like silk, wool, ivory, hair, straw, which are likely to be damaged by chlorine. (iii) It is used for restoring

the colour of oil paintings. In these paints white basic lead carbonate is used, which is turned black by hydrogen sulphide in air. By treatment with hydrogen peroxide it is changed to white lead sulphate. (iv) It is used as a preservatives for milk, wine, etc. (v) It is used as a source of oxygen in rockets. (vi) It is used as an oxidising agent in laboratory.

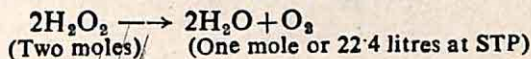
2.14. STRENGTH OF HYDROGEN PEROXIDE SOLUTION

Sometimes the concentration of hydrogen peroxide solution is indicated as mass percentage. Thus, 30% solution of hydrogen peroxide means 30 grams of hydrogen peroxide present in 100 grams of water.

The concentration of hydrogen peroxide is generally expressed as "number volume". It means the number of volumes of oxygen at STP which would be evolved by one volume of hydrogen peroxide solution on heating. Thus, "20 volume" hydrogen peroxide refers to a hydrogen peroxide whose 1 litre on heating would give 20 litres of oxygen at STP.

Example 2.1. What will be the volumetric concentration of 1 M hydrogen peroxide solution?

Decomposition equation for hydrogen peroxide is :



∴ From 2 litres of 1M solution of H_2O_2 the
oxygen available at STP = 22.4 litres

or From 1 litre of 1M solution of H_2O_2 the
oxygen available at STP = $\frac{22.4}{2} = 11.2$ litres

or From 1 ml of 1M solution of H_2O_2 the
oxygen available at STP = 11.2 ml.

∴ Volume concentration of 1M solution = 11.2 volumes.

Example 2.2. Calculate the (i) molarity and (ii) mass percentage of a "10 volumes" hydrogen peroxide solution.

(i) 1 ml of "10 volume" H_2O_2

solution will give = 10 ml of O_2 at STP

But 22.4 litres O_2 at STP \equiv 1 litre of 2M solution of H_2O_2

or 22.4 ml O_2 at STP \equiv 1 ml of 2M solution of H_2O_2

or 10 ml O_2 at STP \equiv 1 ml of $\frac{2\text{M} \times 10}{22.4}$ sol. of H_2O_2
 $\equiv 0.9\text{M}$ solution of H_2O_2

∴ Molarity or molar concentration of "10 volumes"
 H_2O_2 solution = 0.9.

(ii) 1 litre of 0.9M H_2O_2 solution contains

$$= 0.9 \text{ mole } \text{H}_2\text{O}_2$$

$$= 0.9 \times 34 \text{ g } \text{H}_2\text{O}_2$$

$$= 30.6 \text{ g of } \text{H}_2\text{O}_2$$

Supposing the density of the solution is close to one,

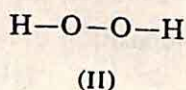
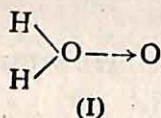
\therefore 30.6 g H_2O_2 will be available in 1,000 grams of solution.

or Percentage of H_2O_2 in solution $= \frac{100}{1000} \times 30.6 = 3.06\%$.

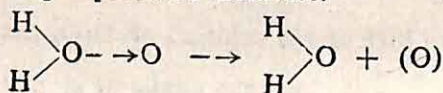
Hydrogen peroxide solution of "10 or 20 volume" concentrations are available in the market. Thus, these contain respectively 3 or 6% H_2O_2 . For chemical requirements solution of "100 volumes strength" is also available. This contains about 30% H_2O_2 by mass.

2.15. STRUCTURE OF HYDROGEN PEROXIDE

The two structural formulae suggested for hydrogen peroxide are :



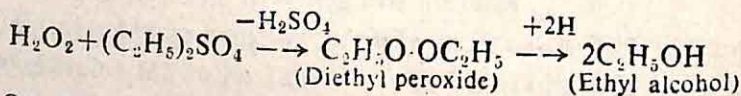
Structure (I) was suggested by Kingett, in the year 1884, on the basis that during oxidation process, only one oxygen atom is lost from the hydrogen peroxide molecule.



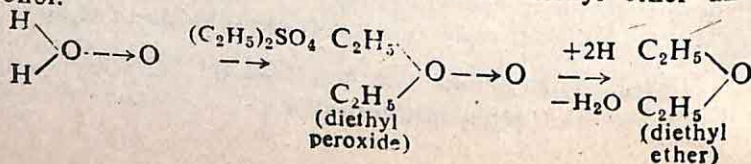
Structure (II) was suggested by Baeyer, in the year 1900. The evidences in favour of dihydroxyl structures are :

(i) Hydrogen peroxide is a weak dibasic acid and gives two series of salts $\text{NaO}-\text{OH}$ and $\text{NaO}-\text{ONa}$. This suggests the presence of two hydroxyl groups in the molecule.

(ii) Hydrogen peroxide reacts with diethyl sulphate to give diethyl peroxide, which on reduction with zinc and acetic acid gives ethyl alcohol.



On the other hand, taking (I) as the structure of hydrogen peroxide the product should have been diethyl ether and not alcohol.

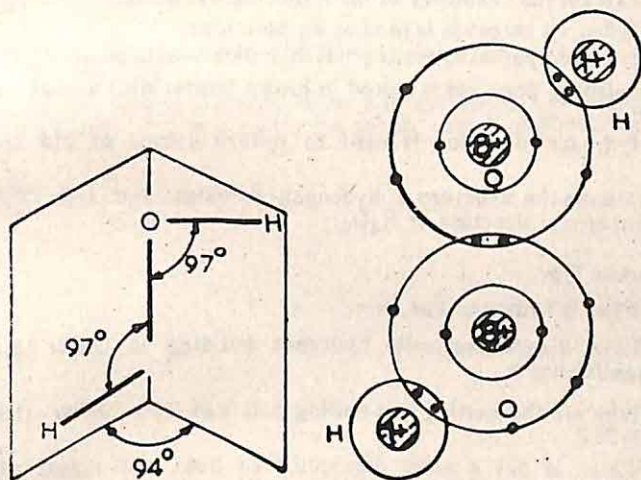


Since in actual practice ethyl alcohol is produced instead of diethyl ether, so, the structure (I) is again ruled out for H_2O_2 .

(iii) X-rays examination of the crystal structures of peroxides of alkali and alkaline earth metals have revealed the presence of the $-\text{O}-\text{O}-$ linkage in H_2O_2 molecule.

(iv) Infra red absorption spectra of anhydrous hydrogen peroxide further confirms structure (II).

(v) The study of dipole moment of hydrogen peroxide indicates a non-polar molecule, which can be best pictured as given below.



QUESTIONS

(A) Essay Type

1. Write a descriptive note on the structure of water molecule. What is it polar?
2. Give reasons for the following :
 - (i) Ice is lighter than water.
 - (ii) Water has maximum density at 277K.
 - (iii) NaCl is soluble in water but CCl_4 is not.
3. How is heavy water prepared? Give some of its important properties and uses.
4. What do you understand by the term 'hard' and 'soft' water? How many types of hardness in water are you familiar with and what are these due to? Give two methods for the removal of each type of hardness and explain the reactions involved.
5. Describe briefly the methods of purifying water for drinking purposes. Is hard water always harmful for drinking? Is soft water always safe for drinking?

2.30 | ESSENTIALS OF CHEMISTRY

6. What are substances that make water hard? Why does hardness of water render it unfit for use in boilers and for washing purposes? How can hard water be rendered suitable for above uses?

7. Describe the principles of ion exchange method of softening hard water?

8. How is hydrogen peroxide prepared in laboratory? Give its important properties and uses.

9. Justify the statement that hydrogen peroxide acts both as an oxidising and reducing agent.

10. How is hydrogen peroxide manufactured by the electrolysis of H_2SO_4 ?

11. Explain the chemistry of the following statements :

(i) Hydrogen peroxide is used as an antichlor.

(ii) Hydrogen peroxide turns potassium dichromate solution green.

(iii) Hydrogen peroxide is stored in brown bottles with a small quantity of acetanilide.

(iv) Hydrogen peroxide is used to restore colour of old faded oil paintings.

12. Discuss the structure of hydrogen peroxide and give evidence in support of dihydroxyl structure of H_2O_2 .

(B) Short Answer Type

13. What is hydrogen bonding?

14. Show diagrammatically hydrogen bonding in water molecule. What is its significance?

15. Why are the melting and boiling points of H_2O higher than those of H_2S and H_2Se ?

16. Water is not a good conductor of heat, still water is used for cooling hot substances and for heating room. Why is it so?

17. Compare the properties of D_2O with H_2O .

18. Why is the use of hard water costly for washing purposes?

19. Why is sea water not used for generating steam in boilers?

20. What are soft and hard waters? What metal ions are responsible for it?

21. How is the strength of hydrogen peroxide reported?

22. How is hydrogen peroxide purified under reduced pressure?

23. What do you understand by a '3 volume' hydrogen peroxide solution?

24. How will you prepare 50% solution of H_2O_2 ?

(C) Problems

25. Determine the mass of hydrogen peroxide present in 400 ml of a "10 volumes" solution of it. (Ans. 12.14 g)

26. Calculate the strength in g/l of a solution of hydrogen peroxide which is marked "60 volumes". (Ans. 18.2 g/l)

(D) Objective Type

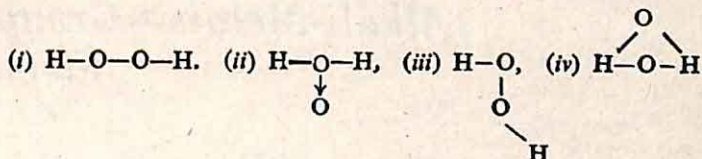
27. Put a tick mark for the correct answer.

(a) Hard water is not very harmful for (i) laundry, (ii) boilers, (iii) drinking, (iv) bathing.

(b) Heavy water is used as a moderator in atomic reactors to slow down the neutrons. Heavy water is (i) a product of oxygen and deuterium, (ii) ordinary water in which the salts of heavy metals are dissolved, (iii) water of mineral springs, (iv) water obtained by repeated distillations and condensation.

(c) Permanent hardness of water may be removed by the addition of (i) lime, (ii) alum, (iii) KMnO_4 , (iv) sodium carbonate.

(d) The correct structural formula of hydrogen peroxide is ;



(e) Mass percentage in 30 volumes H_2O_2 solution is (i) 6.7, (ii) 9.12, (iii) 12.5, (iv) 5.88.

(f) Hydrogen peroxide does not act as (i) a reducing agent, (ii) an oxidising agent, (iii) a dehydrating agent, (iv) a bleaching agent.



Alkali Metals—Group IA Elements

s-Block (Representative Elements)														p-Block (Representative Elements)												
Groups I A														II A III A IV A V A VI A VII A O												
Periods	1	H	1 A																						H	He
	2	Li	Be															B	C	N	O	F	Ne			
	3	Na	Mg	d-Block (Transition Elements)										IB IIB		Al	Si	P	S	Cl	Ar					
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr							
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe							
	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn							
	7	Fr	Ra	Ac	Ku	Ha																				

3.1. GENERAL DISCUSSION

Group IA of the periodic table consists of six elements viz., lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and a newly discovered element francium (Fr). They are highly reactive and form strongly alkaline oxides and hydroxides. Therefore, they are commonly known as *alkali metals*.

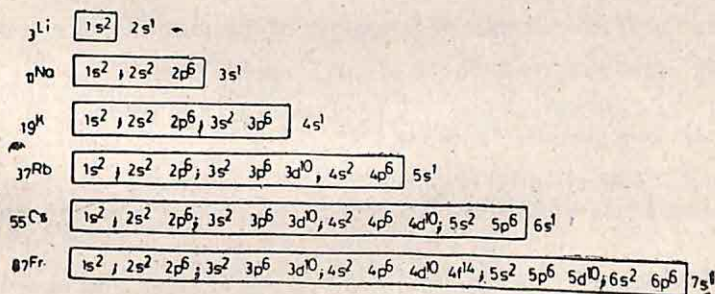
These are s-block elements and have one electron in their outermost orbital. Ignoring the filled inner orbitals their electronic structures are : $2s^1$, $3s^1$, $4s^1$, $5s^1$, $6s^1$, $7s^1$ respectively. Because of their similar electronic structure they resemble closely in their physical properties and chemical behaviour. Francium (Fr) is one of the most recently discovered elements, and very little is known about its properties. Hence, some of the physical properties of only first five members of the group are listed in Table 3.1.

Table 3.1. *Physical properties of alkali metals.*

Property	Li	Na	K	Rb	Cs
Electronic configuration	(He)2s ¹	(Ne)3s ¹	(Ar)4s ¹	(Kr)5s ¹	(Xe)6s ¹
Abundance in earth's crust (ppm)	6.5 × 10 ¹	2.8 × 10 ⁴	2.6 × 10 ⁴	3.1 × 10 ³	0.7 × 10 ¹
Atomic radius (Å)	1.225	1.572	2.025	2.16	2.35
Ionic radius (Å)	0.60	0.95	1.33	1.48	1.69
Ionisation energy (kJ mol ⁻¹)	520	495	418	403	374
Density (g cm ⁻³)	0.53	0.97	0.859	1.53	1.90
Melting point (K)	453	371	337	312	302
Electronegativity	1.0	0.9	0.8	0.79	0.7

3.2. GENERAL CHARACTERISTICS AND TREND OF ALKALI METALS

(A) **Physical Properties.** (i) *Electronic configuration.* The alkali metals belong to the *ns¹* category of elements and hence they are termed as *s-block elements*. Since they have one electron in the outermost shell they have a common valency +1.

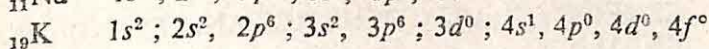
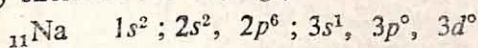


(2) *Atomic size and ionic radii.* The values of atomic and ionic radii of alkali metals, reveal that they possess large atomic size. Also the value of atomic size increases with the atomic number from Li and Cs, since the nuclear charge and the number of energy levels increase.

(3) *Ionisation energy.* On account of the large atomic size the outermost electron in an alkali metal atom is less firmly held. Consequently, the alkali metals possess low ionisation energy (see Table 3.1). This attributes a strong metallic character and high chemical activity of the alkali metals. Their strong tendency to ion formation also indicates that the salts of these metals should invariably exist in well-defined crystalline shapes.

(4) *Reducing agent.* Because the atoms of these elements have great tendency to lose electrons they behave as powerful reducing agents.

(5) *Metallic bond formation.* As already explained the valency electrons are less firmly held in alkali metals. Valency electron normally exists in the s -orbital, while the other orbitals (p , d , f , etc.) of valency shell are vacant, e.g.,



Consequently, the outermost electron can freely move from one atom to the vacant orbitals of another atom leaving the residual atom momentarily positively charged. This type of bond holding the atoms of a metal together is termed *metallic bond*. The metallic bond in the alkali metals is weak because of the mobile and non-localised valency electrons. The weak metallic bond explains the following characteristics of the alkali metals.











- (i) *Soft wax-like texture* because of the mobility of electrons.
- (ii) *Low density* because of large size of atoms.
- (iii) *Electrical conductivity* because of free movement of electrons from one atom to another.

(iv) *Conduction of heat* because of movement of electrons, on heating from regions of high energy to the regions of low energy level.

(v) *Ductility and malleability* because of weak and non-directional metallic bonds.

(6) *Electronegativity.* The electronegativity values for alkali metals are the lowest in the corresponding periods and decrease downwards from lithium to caesium. This indicates the increasing metallic character from lithium to caesium.

(7) *Flame colouration.* The alkali metals and their salts, when introduced in the bunsen flame, impart colours to the flame.

	
Li, 1.23 Å	Li ⁺ , 0.60 Å
	
Na, 1.57 Å	Na ⁺ , 0.97 Å
	
K, 2.03 Å	K ⁺ , 1.33 Å
	
Rb, 2.16 Å	Rb ⁺ , 1.47 Å
	
Cs, 2.35 Å	Cs ⁺ , 1.67 Å

Thus, lithium gives carmine red ; sodium gives golden yellow ; potassium gives pale violet ; rubidium gives violet and caesium gives blue flame. This property offers a very sensitive and reliable test for the alkali metals and is referred to as the flame test. Even 1 part of sodium in 1×10^7 parts can be detected by this test.

(8) *Photoelectric effect.* The low energy photons can eject the loosely held *s*-electron from the surface of these metals. Therefore, these metals, especially caesium, is used in photoelectric cells since they are sensitive to light.

(B) *Chemical Properties.* The ease with which the valency electron is lost in alkali metals makes their chemistry essentially that of their ions, i.e., Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ . An appropriate gradation in chemical behaviour stems again from the simplicity in electronic structures combined with regular increase in the size of their ions, i.e., Li^+ to Cs^+ . Some of the important chemical characteristics are :

(1) *Reactivity.* The alkali metals are extremely chemically reactive so that none of them occur free in nature. They tarnish immediately in moist-air and are soon covered with a thick layer of hydroxide. The reactivity towards most reagents increases in the series with increasing size from lithium to caesium. However, in reaction with non-metals having small atomic volumes (such as H, N and C) the trend is reverse, i.e., lithium being the most reactive.

Reactions. The alkali metals are powerful reducing agents because they lose electron easily.



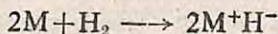
(a) *With water.* They evolve hydrogen violently when added to water causing ignition during the process in case of K, Rb and Cs.



(b) *With alcohol.* They evolve hydrogen when added to alcohol causing ignition in case of K, Rb and Cs.

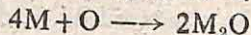


(c) *With hydrogen.* The valency electron of any alkali metal can be transferred to an uncharged hydrogen atom producing salts like hydrides.

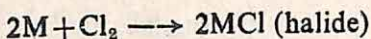


However, the affinity for hydrogen decreases from lithium to caesium.

(d) *With oxygen.* When heated to moderate temperatures in oxygen, the alkali metals ignite forming oxides.



(e) *With other non-metals.* The alkali metals also combine energetically with various non-metals forming ionic compounds such as halides and sulphides.



(f) *Hydration of M^+ ions and conductivity in solution.* The degree of hydration of the alkali metal ions decreases with increasing ionic size. As a consequence, the electrical conductivity in solution decreases from lithium to caesium ion. Lithium, being the most heavily hydrated ion, moves very slowly; and the caesium ion, the least hydrated, moves faster.

(2) *The nature of typical compounds.* (a) *Oxides.* The oxides are all strongly basic and combine with water to form soluble hydroxide (MOH). Their basic character increases from Li to Cs.

(b) *Oxysalts.* Nearly all the alkali metal salts are soluble in water and are thermally stable. With the exception of lithium, all of them form solid bicarbonates ($MHCO_3$) which are readily converted into normal carbonates (M_2CO_3) by gentle heating. The alkali metal carbonates (except Li_2CO_3) do not decompose on heating.

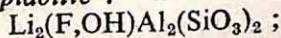
All the alkali metals form hydrogen sulphates ($MHSO_4$) with increasing stability from $LiHSO_4$ to $CsHSO_4$.

The salts of alkali metals, in general, are characterised by high melting point, high conductivity of their melts and ready solubility in water.

3.3. OCCURRENCE OF ALKALI METALS

Because of their high reactivity, none of the alkali metals occur free in nature. The data in Table 3.1 show that Li and Rb are much less abundant compared to Na and K. Fr being radioactive and does not occur in nature.

The important minerals of lithium are *lepidolite* :



Petalite : $LiAl(Si_2O_5)_2$ and *triphylite* $(Li, Na)_3PO_4(Fe, Mn)_3PO_4$.

Sodium occurs as sodium chloride (NaCl) in sea water and as large deposits on earth.

Potassium is found as double salt known as *carnallite* : $KCl \cdot MgCl_2 \cdot 6H_2O$ and as *feldspar* : $K_2O \cdot Al_2O_3 \cdot 6SiO_2$.

Rubidium and *caesium* occur in trace amounts in some aluminosilicates like *lepidolite* and *potlucite* ; $CsAlSi_2O_6 \cdot xH_2O$.

3.4. EXTRACTION OF ALKALI METALS

As mentioned earlier, the metals of this group are strongest reducing agent. Hence, these cannot be prepared by the reduction of their oxides. Also these cannot be prepared by electrolysis of their aqueous solutions, because the liberated atoms at once react with water producing metal hydroxides. Alkali metals are generally extracted by the electrolysis of their fused chlorides. In practice,

the melting points of chlorides are further lowered by adding some other salts. For example, the melting point of sodium chloride is decreased from 1073K to 873K by adding potassium fluoride or potassium chloride to it.

Electrolysis is carried out in steel container, in which a carbon anode is introduced from below. Cathode is made of an iron cylinder which surrounds the anode. An iron wire gauze separates

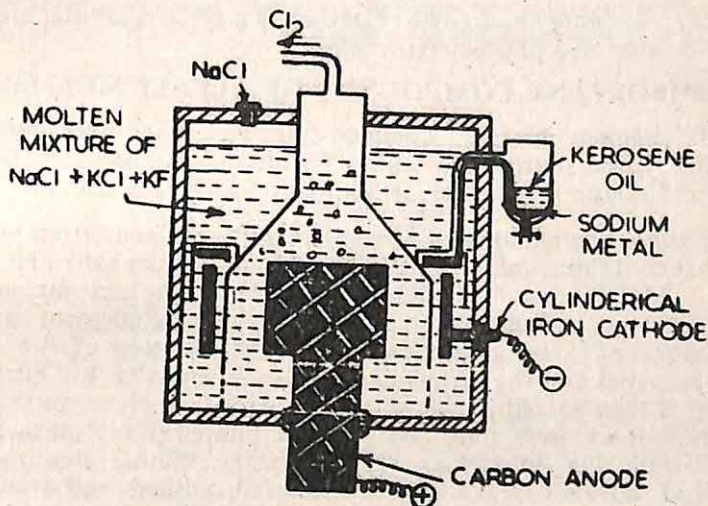
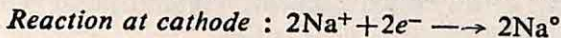


Fig 3.1. Extraction of sodium by electrolysis of fused sodium chloride by down's cell method.

the two electrode areas so that the alkali metal and chlorine produced by electrolysis do not come in contact with each other. For example, when the electrolysis of fused NaCl is carried out (see Fig. 3.1), chlorine is liberated at anode which is led through the hood to a collecting system; and sodium is liberated at the cathode.



Because of the low density of sodium metal, it is forced up through a pipe out of the cell. The metal from the cathode is allowed to cool slowly and is collected in a container filled with kerosene oil. The cell temperature is maintained at about 873K by adjusting the flow of electric current.

3.5. USES OF ALKALI METALS

(1) *Lithium* is used (i) for the manufacture of alloys, (ii) as a deoxidiser in the purification of copper and nickel, (iii) in making a special variety of glass which is very strong and resists weather, (iv) in television picture tubes, (v) in medicine as lithium citrate, and (vi) in air-conditioning plants as lithium chloride.

(2) *Sodium* is used (i) as a reagent in organic analysis and synthesis, (ii) in sodium vapour lamps, (iii) as a reducing agent in

the extraction of titanium, boron and silicon, (iv) for eliminating combined and dissolved oxygen from fused metals, (v) in nuclear reactor as a heat carrier (good conductor of heat), and (vi) in preparation of a number of sodium compounds.

(3) *Potassium* is used (i) in photoelectric cells and (ii) its alloy with sodium is employed for measuring high temperatures, such as of furnaces.

(4) *Rubidium* alongwith *Caesium* is used in the manufacture of radio-tubes and photoelectric cells.

3.6. IMPORTANT COMPOUNDS OF ALKALI METALS

1. Sodium chloride ; Common salt ; NaCl . Sea water and salt beds are richest source of sodium chloride. Some times it is also found in inland lakes, such as Sambhar lake in Rajasthan.

Purification of common salt. The salt obtained from natural source is contaminated with calcium and magnesium salts like CaCl_2 , MgCl_2 , MgSO_4 , etc. The chloride of calcium and magnesium are particularly undesirable on account of their deliquescent nature. For removal of these impurities, a saturated solution of the crude salt is prepared and the suspended matter is removed by filtration. HCl gas is then passed in this solution. Due to increase in the concentration of Cl^- ions, pure NaCl is precipitated out (common ion effect); while the impurities remain in the mother liquor. The crystals of sodium chloride are then filtered, washed and dried.

Properties. It is colourless crystalline solid with "salt-like" taste. It melts at 1073K. It is soluble in water (36g/100g at 293K), the solubility is not changed at higher temperatures. It is almost insoluble in alcohol.

Uses. It is very useful and essential constituent of food that is why it is known as "table salt." It is used for seasoning food and for preserving butter, meat and fish. It is largely used for manufacturing sodium metal, caustic soda, chlorine, sodium carbonate, and many other useful products.

2. Sodium hydroxide ; Caustic soda ; NaOH . It is one of the important heavy chemicals. It was earlier prepared by the causticising process from Na_2CO_3 and Ca(OH)_2 , but now-a-days, electrolytic method has completely replaced it. Electrolytically it can be prepared in a diaphragm cell or a mercury cathode cell. The mercury cathode cell method is described below.

Mercury cathode cell for the manufacture of NaOH . On using mercury cathode the decomposition potential of sodium is considerably lowered due to formation of sodium-amalgam. At the same time the discharge potential for liberation of hydrogen is considerably raised due to overvoltage needs. Consequently, when sodium chloride solution is electrolysed, sodium and not hydrogen is liberated at the mercury cathode, and it is removed in the form of amalgam.

Castner and Kellner designed a cell based on the above consideration. It consists (Fig. 3.2) of a large rectangular trough with a layer of mercury at the bottom. The trough is divided into three compartments, with slate partition short of reaching the bottom of the tank. Thus, mercury in one compartment can flow into the other, but the solutions placed in these compartments can not mix with each other. The cell is kept rocking with the help of an eccentric supporting wheel and thus the mercury is kept in circulation. Graphite anodes are set in the outer compartments filled with salt solution. The middle compartment contains very dilute caustic

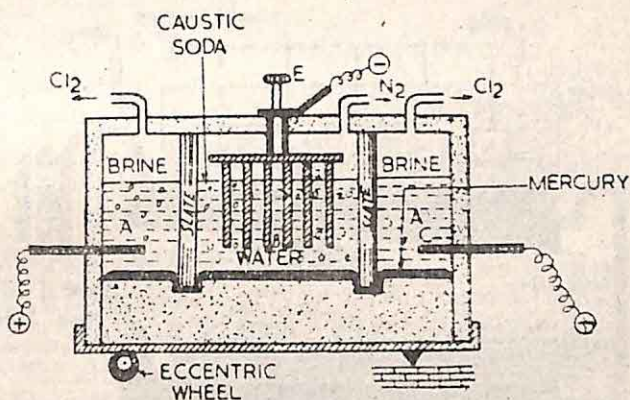
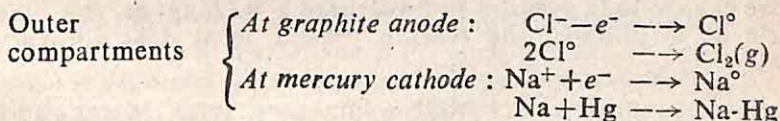


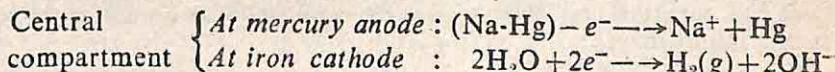
Fig. 3.2. Castner-Kellner cell.

soda solution and is fitted with iron cathodes. By induction, mercury acts as anode in the middle compartment; and as cathode in the outer compartments.

On passing electric current, chlorine is liberated in the outer compartments at the graphite anodes and is let out through exit pipes. Sodium is liberated on mercury cathodes in the outer compartments and forms amalgam with it.



Due to the rocking motion of the tank, sodium amalgam passes from the outer to the middle compartment. In the middle compartment, mercury acts as anode and iron rods act as cathodes. In this compartment the following reactions occur with the formation of sodium hydroxide in solution. Hydrogen liberated at the cathode escapes through a separate exit.



In this way the concentration of Na^+OH^- goes on increasing in the central compartment. When the concentration of caustic

soda solution is reached to about 20% strength, the solution is removed and again replaced by a weak solution.

The caustic soda solution is concentrated by evaporation in multiple effect vacuum evaporators to get fused caustic soda.

Recently, in place of *Castner-Kellner cell* a modified form of cell known as *Kellner-Solvay cell* has been introduced. It has no compartments. Anode is made of graphite rods and is dipped in brine. Cathode is made of mercury which flows continuously at the bottom of the cell (Fig.3.3). The level of the brine is maintained

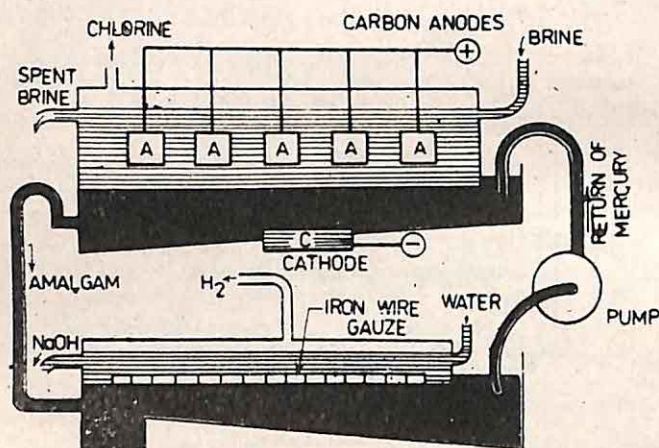


Fig. 3.3. Kellner-Solvay cell.

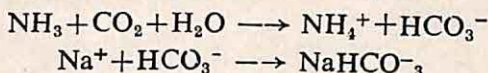
constant. On passing the electric current, chlorine is liberated at the anode and is led out through an exit at the top. Sodium liberated at the mercury cathode forms amalgam with it. Amalgam is carried to another iron vessel containing water (where the amalgam no longer carries any electric charge) and reacts with the latter to give caustic soda solution and hydrogen. So long as the amalgam acts as a cathode, the sodium present in it does not react with water.

Properties. It is a white deliquescent solid. It melts at 591K. It dissolves in water with evolution of heat.

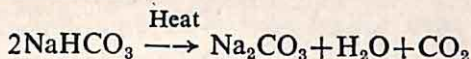
Uses. It is used (i) for manufacturing soap, paper, dye-stuff, artificial silk or rayon, (ii) for preparing sodium salts like hypochlorite, chlorate, nitrite, etc., (iii) for decolorisation and purification of fats and oils, (iv) for absorption of acidic gases, (v) as a good flux for fusion of acidic substances, (vi) in petroleum refining, (vii) for mercerizing cotton fabrics, and (viii) as an alkali reagent in the laboratory.

3. Sodium carbonate ; Washing soda ; Soda ash ; Na_2CO_3 . Now-a-days it is manufactured on large-scale by Solvay ammonia process. The process is based on the principle that when carbon

dioxide is passed through brine (NaCl solution) previously saturated with ammonia, the different available ions in the solution are Na^+ , Cl^- , HCO_3^- and NH_4^+ and the various possible compounds from them are NaCl , NH_4HCO_3 , NH_4Cl and NaHCO_3 . However, out of these, NaHCO_3 is the "least soluble" in water and crystallizes out due to high concentrations of Na^+ and HCO_3^- ions.



The sodium bicarbonate formed is separated and calcined to obtain sodium carbonate.



$\text{CO}_2(\text{g})$ is recirculated and the mother liquor after crystallisation of NaHCO_3 is treated for recovery of ammonia.

The manufacture of sodium carbonate by this method uses only calcium carbonate and sodium chloride as consumable raw materials. Step involved are as follows :

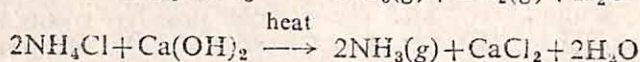
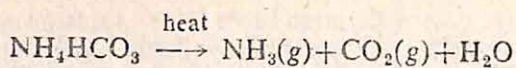
(i) *Saturation of brine with ammonia.* This is done in the ammoniation tower. In this tower a concentrated solution of brine trickles from the top and ammonia gas (from ammonia recovery tower) mixed with a little carbon dioxide enters in the lower-half of the tower. The ammoniacal brine solution thus produced is cooled and sent to the carbonation tower.

(ii) *Carbonation or Solvay tower.* Cooled ammoniacal brine solution is made to flow from the top into the carbonation tower. An excess of carbon dioxide is blown in under pressure from below. Ammonia helps in the formation of bicarbonate ions in the solution. Small crystals of sodium bicarbonate begin to form. Perforated partitions across the tower help in a mixing of the gas with the solution. A sludge of crystals and mother liquor is periodically taken out from the bottom of the tower.

(iii) *Filtration.* The sludge obtained in the Solvay tower is filtered with the help of a vacuum filter pump. The solid sodium bicarbonate is deposited on the surface of the filter cloth and is scrapped off from it at intervals. The mother liquor is pumped to the top of the ammonia recovery tower.

(iv) *Calcination of sodium bicarbonate.* Sodium bicarbonate obtained in the above process is heated strongly when sodium carbonate and carbon dioxide are obtained. Carbon dioxide is sent to the carbonation tower ; and sodium carbonate is packed.

(v) *Ammonia recovery tower.* The filtrate (mother liquor) from the filter pump contains ammonium chloride and a little ammonium bicarbonate. It is made to flow down the ammonia recovery tower alongwith milk of lime. Heating is done by steam pipes. The following reactions take place.



Ammonia (containing some CO_2) pass on to the ammoniation tower. Carbon dioxide required in the carbonation tower is obtained by heating limestone.

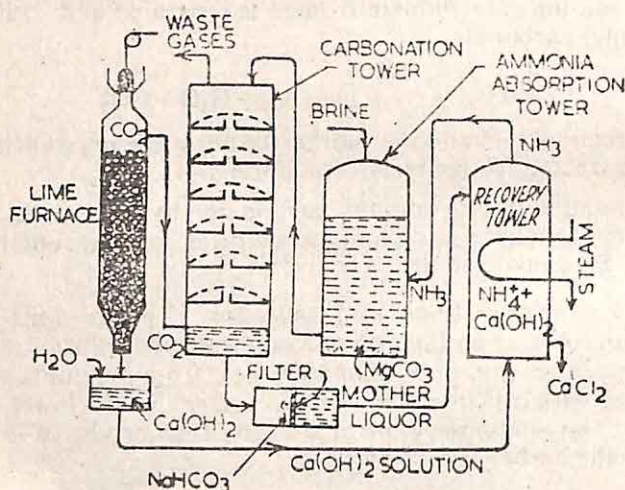
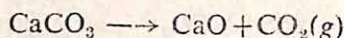
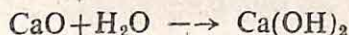
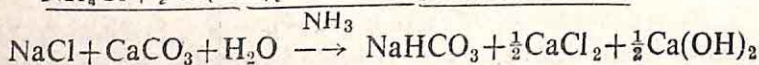
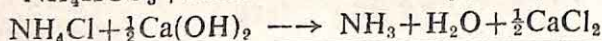
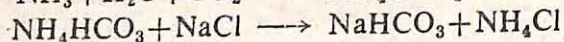
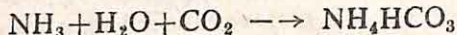
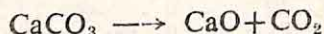


Fig. 3-4. Solvay process.

The residue (CaO) is dissolved in water to produce calcium hydroxide, a part of which is used in the ammonia recovery tower.

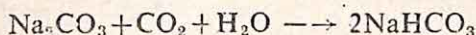


Stoichiometric equations for the process are :



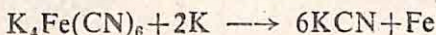
Uses. The sodium carbonate is used (i) in laundry as washing soda and in detergent mixtures, (ii) in the manufacture of caustic soda, sodium silicate and glass, (iii) in water softening for precipitating Ca^{2+} and Mg^{2+} ions, (iv) in textile industry as mild detergent, (v) as a common alkali in making paper pulp, leather tanning and many other industries, (vi) in the laboratory as a reagent providing carbonate ions, (vii) in fusion mixture ($\text{K}_2\text{CO}_3 + \text{Na}_2\text{CO}_3$) for fusing precipitates and minerals.

4. Sodium bicarbonate ; Sodium hydrogen carbonate ; Back-ing soda ; NaHCO_3 . It is made on a large-scale by the Solvay-soda process. An impurity of ammonium bicarbonate in the commercial product can be removed by recrystallising from warm water. Sodium bicarbonate separates as a crystalline precipitate. Crystals are washed with cold water and dried.

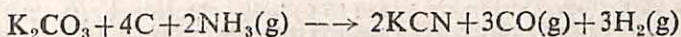


Uses. The sodium bicarbonate is used (i) in medicine to neutralize stomach acidity and in effervescent drinks like fruit salts and seidlitz powder, (ii) for preparing pure sodium carbonate and for the precipitation of normal carbonates of heavy metals, (iii) in the laboratory as bicarbonate reagent, (iv) in fire extinguishers, (weight for weight it gives more CO_2 than sodium carbonate), and (v) in making baking powders.

5. Potassium cyanide ; KCN is prepared by heating potassium ferrocyanide with potassium metal,



or by passing ammonia over fused potassium carbonate containing carbon.



Properties. It is a white crystalline solid, highly soluble in water. It is "deadly poisonous."

Uses. Potassium cyanide is used in electroplating and in the extraction of metals such as silver and gold.

QUESTIONS

(A) Essay Type :

1. Why are the elements of Group IA known as alkali metals? Discuss general characteristics and trend of the elements of this group.

2. Enumerate the main difficulties which arise in the extraction of alkali metals by usual procedures. Describe the extraction of sodium from sodium chloride by Down's process.

3. Describe Castner-Kellner cell for the manufacture of sodium hydroxide. What improvement has been made in this cell by Solvay? List important uses of sodium hydroxide.

4. Describe in detail the manufacture of sodium carbonate by Solvay—ammonia process. Outline the principles involved in this process. Can potassium carbonate be manufactured by this process? Give reasons in support of your answer.

5. Give the preparation and uses of the following compounds. (i) Sodium chloride, (ii) sodium bicarbonate, (iii) potassium cyanide.

6. Give reasons for the following :

(i) Alkali metals do not occur free in nature.

(ii) Lithium cannot be used in photoelectric cells.

(iii) Potassium carbonate cannot be prepared by Solvay process.

7. Which of the following liquids may be used for safe storing of sodium metal and which not? Give reasons : (i) methyl alcohol, (ii) benzene, (iii) diesel oil, (iv) liquid paraffin, (v) acetone, (vi) ethyl ether.

8. How do you account for the gradation in the following properties of the alkali metals.

(i) photo electric effect, (ii) melting point, (iii) density, (iv) ionisation energy, (v) ionic radius.

(B) Short Answer Type :

9. Explain why the alkali metals are soft, low melting and highly reactive ?

10. Why do alkali metals impart colour to flame ?

11. Why do K and Cs find use in photoelectric cell ?

12. Why potassium chloride and potassium fluoride are added in the electrolysis of fused NaCl ?

13. Why is Solvay process not used to manufacture potassium carbonate ?

14. How will you distinguish between NaHCO_3 and Na_2CO_3 ?

15. Name the metal which can be extracted from the following minerals : (i) Lepidolite, (ii) Petalite, (iii) Carnallite, and (iv) potlucite.

(C) Objective Type :

16. Put a tick mark for the correct answer.

(a) During the electrolysis of fused sodium chloride, potassium chloride and potassium fluoride are added to sodium chloride to (i) increase the conductance of fused sodium chloride, (ii) increase the mobility of fused sodium chloride, (iii) facilitate the discharge of Na^+ ions, (iv) lower the fusion point of sodium chloride.

(b) Which one of the following statements is not true for sodium.

(i) It is used in laboratory as a reducing agent in organic reactions.

(ii) It is used for eliminating combined and dissolved oxygen from fused metals.

(iii) It is preserved in water.

(iv) It is used in nuclear reactor as a heat carrier.

(c) Which one of the following statements is not true for sodium hydroxide ? It is used.

(i) in petroleum refining, (ii) for mercerizing cotton fabrics, (iii) as a good flux for fusion of basic substances, (iv) for decolourisation and purification of fats and oils.



Alkaline Earth Metals— Group IIA Elements

		s-Block (Representative Elements)										p-Block (Representative Elements)									
		I A		d-Block (Transition Elements)										III A		IV A	V A	VIA	VII A	O	
Periods	1	H	He											B	C	N	O	F	Ne		
	2	Li	Be																		
	3	Na	Mg	III B	IV B	V B	VIB	VII B	VIII	IB	II B		A	S	P	S	Cl	Ar			
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
	7	Fr	Ra	Ac	Ku	Ha															

4.1. GENERAL DISCUSSION

Group IIA of the periodic table comprises the elements beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). These (except beryllium) are known as *alkaline earth metals*, because the Alchemists gave the name 'earth' to any substance insoluble in water and unchanged by the fire; and the name "alkaline earths" to this group since its oxides (namely lime, magnesia, strontia and baryta) gave alkaline reactions.

These belong to *s-block elements*, having a configuration ns^2 . Because of their similar electronic structures, they resemble closely in physical properties and chemical behaviour. Some of the physical properties of alkaline earth metal along with the electronic configuration are listed in Table 4.1.

Table 4.1. *Physical properties of alkaline earth metals.*

Properties	Be	Mg	Ca	Sr	Ba	Ra
Electronic configuration (He) $2s^2$; (Ne) $3s^2$; (Ar) $4s^2$; (Kr) $5s^2$; (Xe) $6s^2$; (Rn) $7s^2$						
Abundance in earth crust (ppm)	0.6×10^1	2.1×10^4	3.6×10^4	3.0×10^2	2.5×10^2	1.3×10^{-6}
Atomic radius (Å)	0.89	1.36	1.74	1.91	1.98	—
Ionic radius, M^{2+} (Å)	0.31	0.65	0.99	1.13	1.30	1.50
Ionisation energy (kJ mol ⁻¹) E_1	900	738	590	549	502	510
E_2	1757	1450	1146	1060	965	975
Density (g cm ⁻³)	1.80	1.70	1.60	2.60	3.50	5.00
Melting point (K)	1551	924	1116	1062	998	923
Electronegativity	1.5	1.2	1.0	1.0	0.9	0.9

4.1. GENERAL CHARACTERISTICS AND TREND

(A) **Physical Properties.** (1) *Electronic configuration.* All the six elements of group IIA have similar electronic configuration. They have in the outermost shell only *s*-orbital, which contains two electrons. Therefore, they are termed as *s*-block elements and have a common valency, +2.

(2) *Atomic size and ionic radii.* According to the values of atomic and ionic radii given in Table 4.1, the elements of group IIA have large atomic sizes, but smaller than those of the corresponding elements of group IA. In IIA group itself, the atomic size increases from top to bottom as the atomic number (*i.e.*, the nuclear charge) increases and so does the number of the energy levels around the nucleus. This renders the alkaline earth metals highly metallic and electropositive in their behaviour, since the valency electrons are less firmly held on account of the large size of their atoms.

(3) *Ionisation energy.* Like the alkali metals, the alkaline earth metals also have low ionisation energy (Table 4.1), but higher than those of the former. Therefore, the alkaline earth metals are chemically active next to the alkali metals. The low values of their ionization energies also reveal that these elements largely form ionic compounds. Their ionisation energy decreases from Be to Ba.

(4) *Reducing agents.* Since the atoms of these elements have a great tendency to lose electrons, they act as strong reducing agents.

(5) *Metallic bond formation.* Because of the large size of the atoms, the two valency electrons in each of the alkaline earth metals are less firmly held in the *ns* orbital. Also their outermost subshells *p*, *d* and *f* are vacant. Therefore, the valency electrons are in a

mobile state within these orbitals. Hence, the alkaline earth metals possess weak metallic bonds and they exhibit the following properties.

(i) They are *soft* and possess low melting points (m.pt. decreases with increasing atomic number).

(ii) They have *low densities* (density increases with increasing atomic number).

(iii) They are *good conductors of electricity* on account of the free movement of the outer electrons.

(iv) They are *malleable* and *ductile* because the metallic bonds in them are weak and non-directional.

(v) They are *good conductors of heat* because on heating the outer electrons can move to regions of low energy and thus heat is conducted through the entire body of the metal.

(vi) The metals and their salts, when introduced into a bunsen flame, impart *characteristic colour* to it. Thus, Ca gives *brick red*; Sr gives *crimson*; Ba gives *apple green*; Ra gives *carmine red* colours. This is because the electrons can be easily excited to the higher energy states by absorbing small amount of energy. The excited electron when drops back to the original position, emits radiation which fall in visible region of the electromagnetic spectrum and thus appears coloured.

(6) *Electronegativity*. The electronegativity values of alkaline earth metals (except for beryllium) are very low, but not lower than the corresponding values for alkali metals. It decreases with increasing atomic number.

(B) Chemical Properties. (i) *Reactivity*. With the exception of beryllium, the other members have great tendency to give up both valency electrons to form dipositive ions. They are, therefore, highly reactive elements, which is also shown by their position near the alkali metals in the electrochemical series of the elements. The reactivity increases with increasing size of atoms in the group.

(a) *With water*. The reactivity of alkaline earth metals goes on increasing as we go down from Be to Ra. Beryllium is practically unaffected by water at ordinary temperatures; magnesium reacts only slowly with cold water; calcium reacts sluggishly with cold water; strontium rapidly and; barium vigorously.

(b) *With air*. All the elements (except Be and Mg) tarnish quickly in air. When heated strongly, even these metals burn violently. Thus, the tendency to tarnish in air increases downwards in the group.

(c) *With hydrogen*. As the atomic number increases their reactivity towards hydrogen increases, so also the thermal stability of their hydrides, MH_2 .

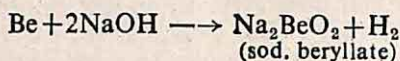
(d) *With nitrogen*. All the members of the group form the nitrides of general formula, M_3N_2 . Stability of nitrides fall with increasing atomic number.

(e) *With oxygen.* The affinity for oxygen increases as we go down the group. The thermal stability, ionic character and solubility of oxides and peroxides increases from Be to Ra.

(j) *With halogens.* They react directly with halogens at appropriate temperatures forming the halides, MX_2 . The reactivity of the metals towards a halogen increases with atomic number. The ionic character and thermal stability of halides increase with increasing atomic number.

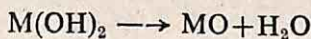
(g) *With acids.* They readily displace hydrogen from dilute acids. The vigour of the reaction increases from Ca to Ra. Beryllium is an exception in being rendered passive by nitric acid.

(h) *With alkalis.* They are not acted upon by alkalis, except beryllium which forms beryllates.



(2) *Nature of typical compounds.* (a) *Oxides.* The oxides are very stable, white solids with high melting points. The oxides are ionic except BeO , which is covalent. The basic character of the oxides increase from BeO to BaO . The oxides tend to react slowly with water and CO_2 in air to form hydroxides and carbonates respectively.

(b) *Hydroxides.* The basic character and solubility of the hydroxides increase from $\text{Be}(\text{OH})_2$ to $\text{Ba}(\text{OH})_2$. The hydroxide give the corresponding oxides on heating.

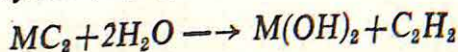


(c) *Halides.* They unite directly with halogens forming halides of the type MX_2 . Beryllium halides (even BeF_2) are covalent, hygroscopic and fume in dry air due to hydrolysis. The halides of other elements of this group are ionic in character and are readily soluble in water.

(d) *Hydrides.* Except Be, they combine directly with hydrogen at very high temperatures to form white, crystalline hydrides of the type MH_2 . The hydrides are ionic, containing the hydride ion, H^- . They are decomposed by water, evolving H_2 . Beryllium hydride cannot be obtained by direct synthesis. Be and Mg hydrides are covalent in character.

(e) *Nitrides.* The nitrides are colourless, crystalline ionic solids (containing N^{3-} ions) and are decomposed on heating. They also react with water giving ammonia.

(f) *Carbides.* They form ionic carbides (or the type MC_2) on heating them or their oxides with carbon. The carbides are ionic compounds [containing the carbide ion, $(\text{C}\equiv\text{C})^{2-}$] and react with water giving acetylene (C_2H_2).



(g) *Carbonates*. The carbonates are insoluble in water and decompose on heating into oxides and carbon dioxide. The stability of the carbonates increases from Be to Ba.

(h) *Sulphides*. Their sulphides are not precipitated by passing H_2S through solutions of their salts. Sulphides are hydrolysed in water and decomposed by dilute acids.

(i) *Sulphates*. Their sulphates are white solids, stable towards heat. The solubility decreases from $BeSO_4$ to $BaSO_4$.

(j) *Peroxides*. Except Be, all form peroxides (MO_2). The peroxides are oxidising agents.

4.3. OCCURRENCE OF ALKALINE EARTH METALS

Because of their high reactivity, none of these metals occur free in nature. The data, in Table 4.1, shows that Be is less abundant as compared to Mg, Ca and Ba. Radium is extremely scarce and is a radioactive element.

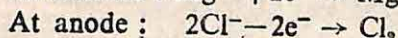
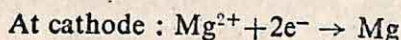
The important mineral of beryllium is *beryl*, $3BeO \cdot Al_2O_3 \cdot 6H_2O$. *Magnesium* occurs as *magnesite*, $MgCO_3$ and *carnallite* $KCl \cdot MgCl_2 \cdot 6H_2O$. *Calcium* is found as *limestone* or *marble* $CaCO_3$; *dolomite*; $CaCO_3 \cdot MgCO_3$ and *gypsum* $CaSO_4 \cdot 2H_2O$. *Barium* occurs as *witherite*, $BaCO_3$; and *barytes*, $BaSO_4$. *Strontium* occurs as *celestine*, $SrSO_4$ and *strontianite*, $SrCO_3$. *Radium* occurs as *pitchblende*—a complex of uranium mineral containing traces of radium.

4.4. EXTRACTION OF ALKALINE EARTH METALS

Like alkali metals, the alkaline earth metals are also strong reducing agents. Therefore, the same difficulties arise during their isolation as were mentioned under extraction of alkali metals. Hence, these metals are usually extracted by the electrolysis of their fused chlorides mixed with alkali metal halide. The latter serves to lower the melting point of alkaline earth metal halide.

Beryllium is extracted by electrolysis of a fused mixture of beryllium chloride and sodium chloride in the ratio of 2 : 1 in a water-cooled nickel crucible (which acts as a cathode) containing carbon rod (which acts as anode).

Magnesium is extracted by electrolysis of a fused mixture of anhydrous magnesium chloride and sodium chloride in the ratio of 7 : 3 in an iron vessel (which serves as cathode) containing a graphite rod (which acts as anode). The graphite rod is surrounded by a porcelain tube, through which the liberated chlorine gas escapes out and hence does not come in contact with magnesium (Fig. 4.1). The temperature of the vessel is maintained at about 970K. The electrolytic reactions are :



Molten magnesium, being lighter than the molten electrolyte, rises and floats at the surface. It is periodically removed with per-

forated ladles. To avoid the oxidation of molten magnesium, the electrolysis is carried out in an inert atmosphere of coal gas.

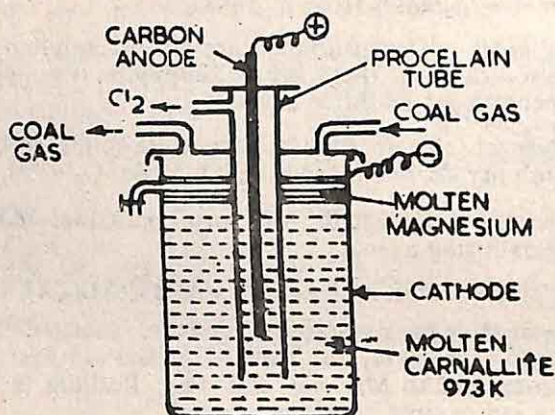


Fig. 4.1. Extraction of magnesium by electrolytic process.

Calcium is extracted by the electrolysis of a fused mixture of calcium fluoride and calcium chloride in the ratio of 1:6:10 in an iron crucible, lined inside with graphite, which also serves as anode. Cathode is a hollow tube of iron, which is water-cooled. The cathode can be moved up and down with the help of screw and socket motion. (Fig. 4.2).

During electrolysis, calcium is deposited on the cathode. As the metal accumulates, the cathode is raised. The calcium metal is obtained as a rod. The lower end of it is dipped in the fused melt and acts as a cathode. Water is circulated around the cathode so that the discharged calcium is deposited in the form of a solid metal. The electrolytic reactions are :

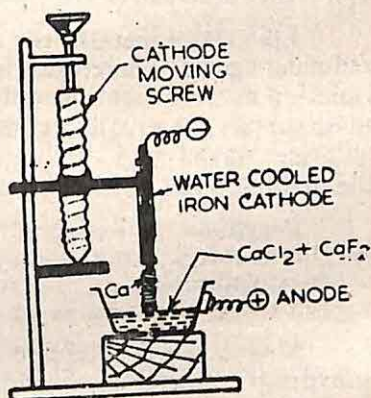
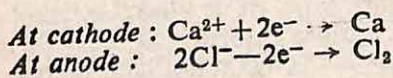
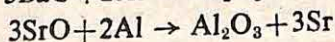


Fig. 4.2. Extraction of calcium.

Chlorine is obtained as a by-product.

Barium and Strontium may be obtained by the reduction of their oxides with aluminium at 1500K.



Radium is extracted by the electrolysis of fused radium-chloride using mercury cathode, when radium-mercury amalgam is produced. Radium is then obtained by distilling off mercury.

4.5. USES OF ALKALINE EARTH METALS

(1) **Beryllium** and its oxide are used in nuclear reactors. The windows of X-ray tubes are made of this metal because it is transparent to these rays due to its low density. Beryllium alloys are used in the manufacture of high strength springs.

(2) **Magnesium** is used (i) in the preparation of alloys. Magnalium (which contains 5 to 15% magnesium and 85 to 95% aluminium) is hard, tough and light. It can be easily worked on lathe and is used for making balance beams and other instruments. Electron (contains 95% Mg and 5% Zn) is used in the construction of the aircraft bodies ; (ii) in the preparation of magnesium wire, ribbon and flash light powders, which are used in photography and fire works ; (iii) for developing high vacuum in radio valves. The last traces of oxygen and nitrogen are absorbed by vaporising magnesium inside the valves ; (iv) for preparing Grignard reagents, which are used for the synthesis of organic compounds.

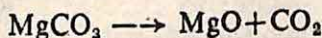
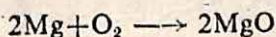
(3) **Calcium** is used (i) for removing last traces of oxygen and nitrogen from noble gases like argon ; (ii) for removal of sulphur from petroleum ; (iii) in producing rigidity to lead alloys ; (iv) in the preparation of hydrolyth, which is used as source of hydrogen ; (v) In reducing oxides which cannot be reduced with carbon, since it is a powerful reducing agent.

(4) **Barium** is used in removing last traces of oxygen and nitrogen from vacuum tubes.

(5) **Radium** salts are used in the treatment of cancer (radio-therapy).

4.6. IMPORTANT COMPOUNDS OF ALKALINE EARTH METALS

(1) **Magnesium oxide, MgO.** *Preparation.* It is prepared either by burning magnesium in air or calcining natural magnesite (MgCO_3) in a kiln.



Note : The oxide formed by burning Mg in air may contain a small impurity of nitride. As oxygen is more reactive than nitrogen, more of MgO is formed even though air contains more nitrogen than oxygen.

Uses. (i) Because of its very high melting point it is used in manufacturing infusible crucible, fire-bricks and other refractory materials for lining electric furnaces ; (ii) Mixed with asbestos powder it gives a fluffy powder. It is used for heat lagging of steam pipes and boilers ; (iii) In sealed wire electric heaters, MgO is filled between the hot wire and the casing as electrical insulator ; (iv) It is used in medicine as purgative ; (v) In flocculant form it is used as filler for rubber ; (vi) It is used in Sorel's cement.

(2) **Magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.** *Preparation.* Anhydrous salt may be prepared by passing chlorine over heated magnesium.



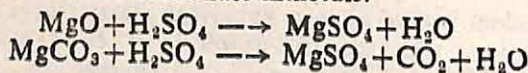
The hydrated salt, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, is obtained by dissolving, MgO or magnesium carbonate in hydrochloric acid. The solution is vaporised to obtain crystals. On a large scale it is prepared by fractional crystallisation of fused carnallite, $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

Uses : (i) In cotton dressings for surgery. (ii) In dental filling pastes and Sorel's cement.

(3) **Magnesium sulphate (Epsom salt), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.** In nature magnesium sulphate occurs as *kieserite*, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ and *epsom salt*, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

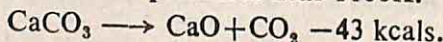
Preparation. (i) The crystals of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ are formed when a saturated solution of *kieserite* is cooled.

(ii) It may be prepared by the action of dilute sulphuric acid on magnesium oxide or carbonate minerals.



Uses : (i) In medicine as a saline purgative and anti-convulsant. (ii) In dyeing and tanning process, in dressing or loading cotton goods and in sizing paper. (iii) For fire-proofing textiles and wood. (iv) As a catalyst in Schoder-Grillo process for the manufacture of sulphuric acid.

(4) **Calcium oxide, Quicklime, CaO .** *Preparation.* It is prepared by calcining limestone at temperatures near 1100K.



The reaction is reversible and CO_2 should be removed to favour the forward reaction. Since the reaction is endothermic, so a rise in temperature will favour forward reaction. However, the temperature should not be allowed to rise above 1270K. At higher temperatures silica present as impurity in limestone will combine with calcium oxide to produce a fusible silicate, which is deposited in the pores of lime. The time thus obtained is slaked with difficulty.

On a commercial scale it is prepared in a specially designed kiln (Fig. 4.3.) Here CO_2 is removed as soon as formed. Calcium oxide is collected from bottom.

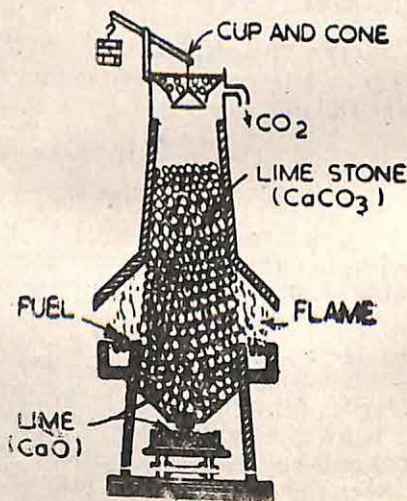
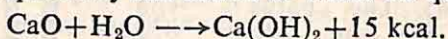


Fig. 4.3. Modern continuous kiln for manufacturing lime.

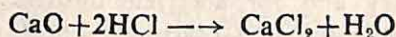
Uses : (i) In the preparation of cement, glass and building mortar. (ii) In the preparation of slaked lime and calcium carbide. (iii) For producing lime light and for drying alcohol and. (iv) As a basic lining in furnaces and as a flux in metallurgy to remove silica.

(5) **Calcium hydroxide or Slaked lime, Ca(OH)_2 .** *Preparation.* Slaked lime is prepared by the action of water on quicklime.



Uses : (i) In white washing, in softening hard water by precipitating bicarbonates and in tanning as a cheap alkali for loosening hair. (ii) As a disinfectant in public places and in medicine ; (iii) For making soil alkaline. (iv) In neutralizing acidic sugar juice and coagulating suspended impurities.

(6) **Calcium Chloride $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$.** *Preparation.* It can be prepared in laboratory by the action of hydrochloric acid on calcium oxide (lime) or carbonate.

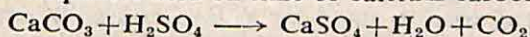


On evaporating the solution calcium chloride is obtained as crystal of hexahydrate ($\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$).

Anhydrous crystals are obtained by heating hydrated crystals strongly.

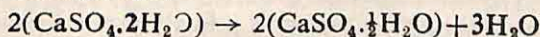
Uses : (i) As a dehydrating agent ; (ii) In preparing freezing mixture with ice and an antifreeze solution in ice making machines; (iii) For making combustible articles, fire-resisting.

(7) **Calcium Sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.** In nature it is found as gypsum or alabaster ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). It may be prepared by the action of dilute sulphuric acid on lime or calcium carbonate.



Uses : It is mainly used in preparing plaster of paris.

(8) **Plaster of Paris, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.** *Preparation.* When gypsum is heated to about 390K, it is changed to the plaster of Paris, a semi hydrate form, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.



If heated to 573K, it loses water of crystallisation completely and is then known as *dead burnt plaster*.

Uses : (i) In surgical bandages for setting broken bones. (ii) In casting molds and statues. (iii) For preparing printing and writing papers from porous paper, and for making good quality mortar.

(9) **Calcium carbide, Calcium acetylide, CaC_2 .** *Preparation.* On a large-scale it is prepared by heating strongly a mixture of calcium oxide and powdered coke in the ratio 2 : 3 in an electrical furnace to a temperature over 2300K.



The furnace is made of iron sheets, lined inside with gas carbon and a block of graphite fixed at the bottom forms one of the electrodes. The other electrode is formed by carbon rods (Fig. 4.4) The charge is poured from the top. When electric current is passed, a temperature of about 2300K is developed and calcium carbide is produced. The molten carbide is taken out from lower hole.

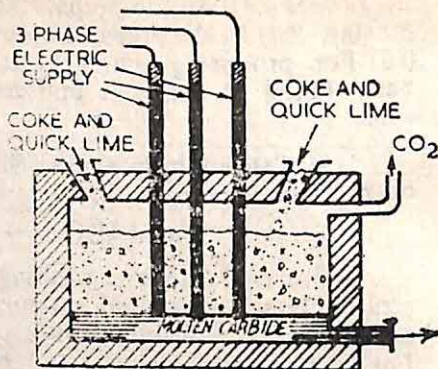
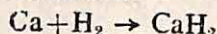


Fig. 4.4. Manufacture of calcium carbide

Uses : (i) In the preparation of acetylene gas which is needed for plastics industry and for acetylene burners. (ii) In the manufacture of nitrolim ($\text{CaCN}_2 + \text{C}$) fertilizers. (iii) As a reducing agent at high temperatures.

(10) Calcium hydride, CaH_2 . It is prepared by passing hydrogen over calcium heated to 670K.



Uses : Under the name *hydrolith* it is used as a source of hydrogen (1 g of it with water yields 1070 ml of the gas at STP).

(11) Portland Cement. Cement is one of the most important building materials. It was first introduced in 1824 by J. Aspedin, a mason of Leeds in England. He found that when a strongly heated mixture of limestone and clay was mixed with a small amount of water and allowed to stand for a few hours, it sets to a stone-like mass. This stone-like mass resembled Portland rock, a famous building stone of England. Thus cement, as described above, was given the name of Portland cement. It is a strongly heated product of a mixture of lime, silica, alumina and iron oxide. Lime (CaO) comes from the limestone; silica (SiO_2), alumina (Al_2O_3) and iron oxide (Fe_2O_3) are contributed by the clays used. It is more often called simply cement. Cement is a finely ground powder of greenish-grey colour. Its main constituents are (1) dicalcium silicate $2\text{CaO} \cdot \text{SiO}_2$, (2) tricalcium silicate, $3\text{CaO} \cdot \text{SiO}_2$, (3) tricalcium aluminate, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, (4) tetracalcium aluminoferrite, $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. Silicates and aluminates of calcium constitute about 90 per cent of the cement. Of these the most abundant constituent is the tricalcium silicate.

The average composition of portland cement is : $\text{CaO} = 50-60\%$; $\text{SiO}_2 = 20-25\%$; $\text{Al}_2\text{O}_3 = 5-10\%$; $\text{MgO} = 2-3\%$; $\text{Fe}_2\text{O}_3 = 1-2\%$ and $\text{SO}_3 = 1-2\%$. For good quality cement, the ratio of silica (SiO_2) to alumina (Al_2O_3) should be between 2.5 and 4 and the ratio of lime (CaO) to the total of oxides of silicon (SiO_2), aluminium (Al_2O_3) and iron (Fe_2O_3) should be as close to 2 as possible.

Manufacture. The raw materials are first crushed either dry or better mixed with proper proportion of water to get a thin mud or slurry (containing about 38 to 40 percent water). The creamy slurry (or the dry mixture) is fed at the upper end of a long rotary kiln. The modern cement kiln consists of a fire-brick lined rotary steel cylinder, 30 to 150m long and 2 to 5m in diameter. It is capable of being slowly rotated about an axis slightly inclined (about

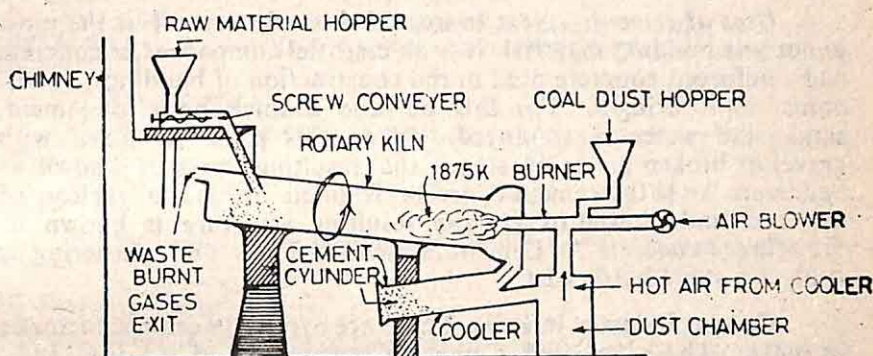


Fig. 4.5. Rotary cement kiln.

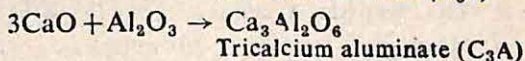
1 m in 20 m of length) to the horizontal. Burning fuel (usually powdered coal or oil) and air are injected at the lower end. A 15m flame is produced, which heats the interior of the kiln to about 1800K. Due to the slope and the slow rotation of the kiln (about 30 rotation per hour) the material fed in moves continuously towards hottest end at a speed of approximately 15m per hour. As the mixture or slurry gradually descends the temperature rises.

(i) In the upper part of the kiln, where the temperature is about 675K, the most of the water in the slurry dries up.

(ii) In the central part of the kiln (about 1275K), limestone decomposes to quicklime and carbon dioxide.



(iii) In the lower part of the kiln, the lime and clay undergo chemical interaction yielding calcium aluminates and silicates.



(iv) These aluminates and silicates then combine together to form small (about 1.25cm in diameter) hard greyish stones (called, *clinkers*).

The glowing hot clinker (at about 1457K) is allowed to cool in revolving steel coolers, in which air is admitted in opposite direction. The hot air so produced is utilised for drying coal before pulverization. The cooled clinker is then pulverized as fine as possible, since the finer the cement the greater is the strength of the concrete made from it. During the final grinding about 2 to 3 per cent of gypsum is added, whose presence prevents too rapid setting of the cement-water paste.

Uses of cement. Next to iron and steel, cement is the most important building material. It is an essential component of concrete and reinforced concrete used in the construction of buildings, roads, dams and bridges. For this purpose a thick paste of cement, sand and water is employed. When this paste is mixed with gravel or broken pieces of stone, the resulting mass is known as "concrete." If the cement concrete is filled around a skeleton of iron rods and allowed to set, the resulting structure is known as "reinforced concrete." Cement is used for floors and plastering as it gives a stone-hard crust.

Cement Industry in India. There are over forty cement factories in India. The associated Cement Companies Ltd. (A.C.C. Ltd.) and Dalmia group are the two largest cement production private concerns. The former runs 14 factories and the latter runs 7 factories. A few factories have been started recently in public sector also. Most of the cement factories are located in Uttar Pradesh, Madhya Pradesh, Bihar, Rajasthan, Andhra, Mysore, Orissa and Gujarat. The production of cement increased considerably from 2.7 million tonnes in 1950-51 to 40 million tonnes in 1977-78.

QUESTIONS

(A) Essay Type

1. Why are the elements of group IIA known as alkaline earth metals? Discuss the general trends of the elements of group II A.
2. How do you account for the gradation in the following properties of the alkaline earth metals.
 - (i) Size of atoms and ions; (ii) ionization energy; (iii) reducing property; (iv) electropositive character.
3. Compare and contrast the properties of alkaline earth metals with those of alkali metals with reference to the following properties.
 - (i) Electropositive character; (ii) density; (iii) ionisation energy, (iv) reducing behaviour; (v) flame spectra.
4. Write equations showing the reactions of a typical IIA group metal with hot water, dilute sulphuric acid and oxygen.
5. Give preparation and uses of the following compounds.
 - (i) Magnesium chloride; (ii) quicklime; (iii) calcium carbide; and (iv) plaster of Paris.
6. How is calcium extracted? Give a diagram of the apparatus used. List some important uses of metallic calcium.
7. What are the important ores of magnesium? Describe the method of extracting the metal. Starting from the metal, how will you prepare its oxide, chloride and sulphate.

8. Complete the following reactions.

- (i) $\text{CaC}_2 + \text{H}_2 \rightarrow$
- (ii) $\text{Ca}(\text{OH})_2$ (cold and hot) + $\text{Cl}_2 \rightarrow$
- (iii) $\text{CaCl}_2 + \text{NaHCO}_3$ (cold and hot) \rightarrow
- (iv) $\text{MgSO}_4 + \text{Na}_2\text{CO}_3$ (soln : fusion) \rightarrow

9. Describe the effect of strong heating on the following :

- (i) $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.
- (ii) Na_2CO_3 and CaCO_3 .
- (iii) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

10. What are the essential constituents of cement ? Draw a neat and labelled diagram for manufacturing the cement. What is the purpose of adding gypsum to it ?

11. Explain why :

- (i) the aqueous solution of an alkaline earth metal cannot be electrolysed ;
- (ii) the chemical reduction of an alkaline earth metal salt is not feasible ; and
- (iii) the fused alkaline earth metal chlorides are electrolysed in presence of NaCl ?

(B) Short-Answer Type

12. Name the elements of Group IIA. Give their electronic configurations.

13. Why are the alkaline earth metals harder, denser and higher temperature melting compared to the corresponding alkali metals ?

14. Why the alkali metals do not occurs free in nature ?

15. Why is lime sprinkled in the fields ?

16. Why is calcium chloride solution sprinkled on dusty roads ?

17. Why is calcium chloride sprinkled on snow covered roads ?

18. Why is a flame produced when magnesium is burnt ? What other metal would you expect to burn with a flame ?

19. Name the metal which can be extracted from the following compounds : fluorspar, barytes, beryl, kainite, gypsum and carnallite.

20. What are the general trends in the solubilities of the following alkaline earth salts (a) sulphates, (b) hydroxides ?

(C) Objective Type

21. Put a tick mark for the correct answer.

(a) Formula of plaster of Paris is (i) CaSO_4 ; (ii) $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$.
(iii) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$; (iv) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

(b) The colour imparted by strontium salt to the bunsen burner flame is i) blue, (ii) light pink, (iii) green, (iv) crimson.

(c) Calcium is prepared by the electrolysis of (i) fused anhydrous calcium chloride ; (ii) calcium chloride solution ; (iii) calcium hydroxide ; (iv) calcium phosphate.

(d) Formula of dead burnt plaster is (i) $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$; (ii) $2\text{CaSO}_4 \cdot \text{H}_2\text{O}$; (iii) $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$; (iv) CaSO_4 .

(e) Chemically nitrolim is (i) $\text{CaC}_2 + \text{O}_2$; (ii) $\text{CaCN}_2 + \text{C}$; (iii) $\text{Ca}(\text{CN})_2 + \text{C}$; (iv) CaC_2 .

(f) The initial setting time of cement is regulated by the addition of (i) alum ; (ii) green vitrol ; (iii) gypsum, (iv) blue vitriol.

Boron and Aluminium- Group IIIA Elements

		s-Block (Representative Elements)										p-Block (Representative Elements)									
		I A												VII A		0					
Periods	Groups	I A		d-Block (Transition Elements)										II A		III A					
	1	H	II A											B	C	N	O	F	Ne		
	2	Li	Be																		
	3	Na	Mg	III B	IV B	V B	VI B	VII B	VIII		IB	II B		Al	Si	P	S	Cl	Ar		
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
	7	Fr	Ra	Ac	Ku	Ha															

5.1. GENERAL DISCUSSION

Group IIIA of the periodic table comprises of elements boron (B), aluminium (Al), gallium (Ga), indium (In) and thallium (Tl). These elements are characterised by their configuration ns^2, np^1 . Thus, these elements belong to p -block elements. Electronic configuration and some of the physical properties of elements of this group are listed on next page.

5.2. GENERAL CHARACTERISTICS AND TREND

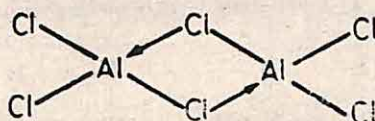
(A) **Physical Properties.** (1) *Electronic configuration.* Table 5.1. reveals that B, Al, Ga, In and Tl possess similar electronic configurations since they all have 3 electrons in the outermost shell, which is further split up into ns^2 and np^1 orbitals.

(2) *Electropositive character.* The electropositive character increase from boron to aluminium and then decreases from aluminium to thallium. The increase from B to Al is due to the usual increase in atomic size, since they follow immediately the s -block elements Be, Mg respectively. On the other hand, Ga, In and Tl follow the d -block elements Zn, Cd and Hg respectively. The extra d -electrons in case of Ga, In and Tl do not shield the nuclear charge very effectively, so, the orbital electrons are held more firmly and consequently they are less electropositive than Al.

Table 5.1. Physical properties of group IIIA elements.

Property	B	Al	Ga	In	Tl
Electronic configuration	(He) $2s^2, 2p^1$;	(Ne) $3s^2, 3p^1$;	(Ar) $3d^{10}, 4s^2, 4p^1$;	(Kr) $4d^{10}, 5s^2, 5p^1$;	(Xe) $4f^{14}, 5d^{10}, 6s^2, 6p^1$
Abundance (ppm.)	1.0×10^1	8.13×10^4	1.5×10^1	0.1×10^1	0.3×10^1
Atomic radius (Å)	0.80	1.25	1.26	1.44	1.48
Ionic radius, M^{3+} (Å)	0.20	0.50	0.60	0.81	0.95
Ionisation energy (kJ mol ⁻¹)					
I	800	577	579	558	589
II	2427	1816	1979	1820	1970
III	3658	2745	2962	2703	2879
Density (g/cm ³)	2.30	2.70	5.93	7.29	11.85
Melting point (K)	2573	933	303	429	576
Boiling point (K)	2823	2740	2676	2273	1730
Electronegativity	2.0	1.5	1.6	1.7	1.8

(3) *Ionisation energy.* Because of high ionisation energies, B and Al generally form covalent compounds. In these compounds the central elements contain only three electron pairs as in BCl_3 , AlCl_3 , etc. They are thus electron deficient compounds and can accept electrons from other donor molecules to achieve the stable configuration (ns^2, np^6) of the next noble gas. For example, BCl_3 accepts a pair of electrons from NH_3 to form $\text{H}_3\text{N} \rightarrow \text{BCl}_3$. Aluminium chloride exists as dimer, (Al_2Cl_6) in which each Al atom acquires an octet by accepting a lone pair of electrons from Cl atom. The structure is shown below.



Similarly, in the formation of K^+BF_4^- or $\text{Li}^+\text{AlH}_4^-$ the central atom acquires the stable configuration.

(4) *Metallic character.* Only boron is non-metal. All other elements of group IIIA are fairly reactive metals. Boron shows resemblance with the diagonally related element, silicon in the next group. Both boron and silicon, thus, form similar type of compounds.

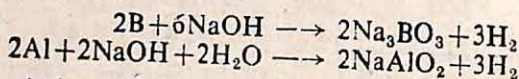
On examination of Table 5.1 we observe that densities and atomic sizes of these elements gradually rise with increase in atomic number from boron to thallium. But in case of melting points,

there is sudden fall down from aluminium to gallium followed by gradual rise again to thallium. The melting point of boron is extremely high, indicating strong bonding between individual atoms. The melting points of other elements, especially, Ga, In and Tl, are significantly low indicating that the metallic lattices in these are much more readily ruptured. Their boiling points are high and decrease, in general, with increasing atomic number.

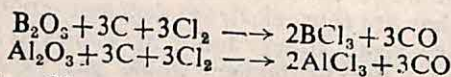
(B) **Chemical Properties.** (1) *Action with air.* The five elements have varied standards of reactivity. Amorphous boron, being impure, burns in air forming its oxide (B_2O_3) and nitride (BN). Pure crystalline boron, however, is unreactive. The metals Ga, In and Tl are stable in air. Aluminium, however, is coated with protective oxide film on its surface.

(2) *Action with acid.* Boron in presence of impurities is attacked by concentrated sulphuric and nitric acids. It does not react with non-oxidising acids (HCl, etc). On the other hand, Al, Ga and In dissolve in acids to form trivalent ions (M^{3+}). Thallium, however, dissolves in acid to form Tl^+ ion.

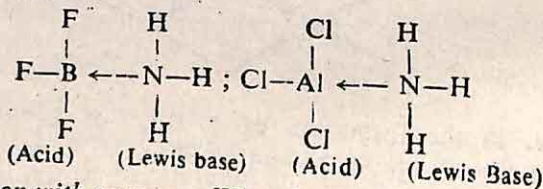
(3) *Action with alkalis.* They all dissolve in alkalis evolving hydrogen gas, e.g.,



(4) *Action with halogens.* They form trihalides (of the formula MX_3) by direct combination with halogens. The chlorides can be obtained by heating their oxides with charcoal in a current of chlorine, e.g.,



The halides of boron are covalent and are hydrolysed by water. The halides of aluminium (except AlF_3) are also covalent when anhydrous and are partially hydrolysed with water. Boron and aluminium atoms in their halides are two electrons short of a noble gas electronic configuration. They possess, therefore, marked electron acceptor (Lewis base) properties with suitable donors (Lewis acid), e.g.,



(5) *Action with oxygen.* When heated in oxygen, they form oxides of the general formula M_2O_3 .

5.3. OCCURRENCE OF BORON

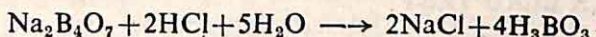
Being reactive, boron does not occur free in nature. In combined state it is found as ;

(1) **Borax**, $Na_2B_4O_7 \cdot 10H_2O$ (found in India, Tibet, Ceylon and California)

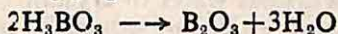
- (2) Kernite, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ (found in California)
 (3) Colemanite, $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$ (found in California and Chile)
 (4) Boric acid, H_3BO_3 (found in the hot springs of Italy's volcanic region).

5.4. EXTRACTION OF BORON

It is isolated by the reduction of boric anhydride (B_2O_3) with a strongly electropositive metal (e.g., Na, K, Mg). The boron trioxide is obtained from colemanite or borax. A hot saturated solution of borax is treated with concentrated HCl to obtain crystals of boric acid.



Then, boric acid is strongly ignited to obtain boric anhydride.



Reduction of boric anhydride. Excess of B_2O_3 is mixed with magnesium powder and heated to bright redness.

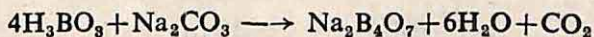


The residual mass is broken up and boiled with concentrated HCl to dissolve out MgO and excess of B_2O_3 , when a dark-brown powder of amorphous boron is obtained as residue.

5.5. BORAX, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.

Preparation. (i) *From native borax (tincal) or kernite.* Crude borax (tincal) or kernite are sodium tetraborates and constitute the main source of borax. The crude ore is treated with hot water when borax dissolves, leaving behind the insoluble impurities. The crystals of the composition, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ separate out on cooling and concentration of clear solution.

(ii) *From boric acid.* Boric acid is deposited when water from certain hot springs in Italy cools. When a solution of acid is treated with calculated amount of sodium carbonate, borax is formed.



Uses. (i) In the borax bead test for the identification of Ni^{2+} , Co^{2+} , Fe^{3+} , Cr^{3+} and Mn^{2+} . (ii) As a flux in welding and soldering of metals by removing oxides from their surfaces and thus bringing the fresh metals together for a strong weld. (iii) In making borosilicate glassware (Pyrex and Jena) that are very resistant to heat and shock. (iv) To clean hides in tanning, as a mordant for both leather and textiles, and to remove gum from raw silk.

5.6. BORIC ACID (ORTHOBORIC ACID), H_3BO_3

Preparation. (i) *From borax.* When a hot concentrated solution of borax is mixed with hydrochloric acid and the liquid allowed to cool, crystals of boric acid separate out.

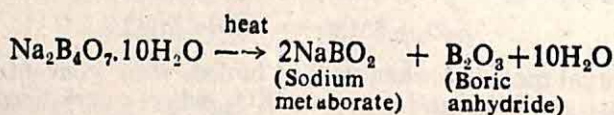


(ii) *From Soffoni.* Boric acid is contained in the jets of stream (or soffoni) which issue from the ground in volcanic regions in tuscany (Italy). These are passed through large tanks of water called 'lagoons'. The resulting solution is concentrated by steam and cooled when pure boric acid crystallises out. It is recrystallised from water once or twice to give pure boric acid.

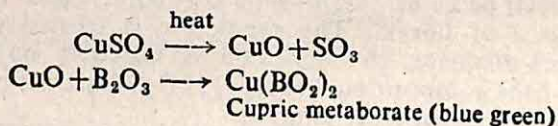
Uses : (i) As an antiseptic in medicine. (ii) In making enamels and potency glazes. (iii) In glass industry and in preservation of good.

5.7. BORAX BEAD TEST

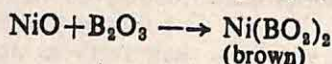
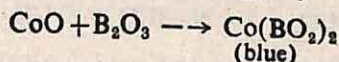
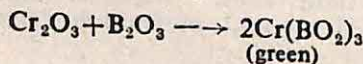
This test is used to identify the coloured salts cations. When borax is heated, it fuses, loses water of crystallisation and swells up into a white porous mass, which subsequently melts into a clear transparent glassy bead consisting of sodium metaborate and boric anhydride.



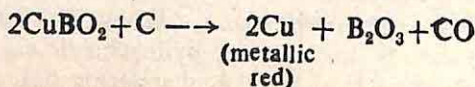
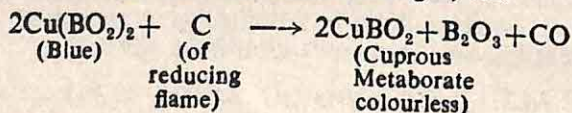
When this bead is heated with coloured mixture of salts, a characteristic coloured bead of metaborate is formed. Thus, with copper salt a bluish-green cupric metaborate is obtained in 'oxidising flame'.



Likewise, chromium, cobalt, nickel, etc. give metaborates having characteristic colours in oxidising flame.

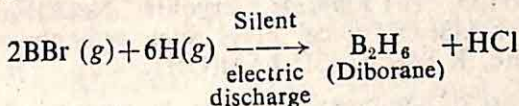


However, in reducing flame the colour changes, viz.



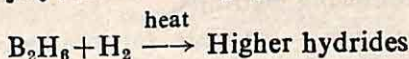
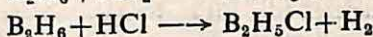
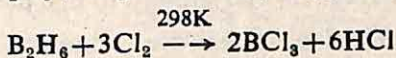
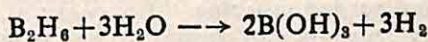
5.8. BORON HYDRIDES

Boron forms hydrides (also known as boranes) of the general formula B_nH_{n+6} and B_nH_{n+4} . They were earlier prepared by treating magnesium boride with hydrochloric acid. Now-a-days, diborane is prepared by submitting a mixture of boron triboride and excess of hydrogen to silent discharge at a pressure less than 10 mm of Hg.

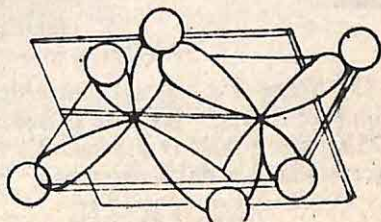
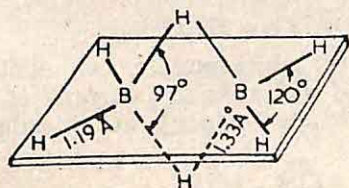


Other hydrides of boron are obtained from diborane by cracking or by heating diborane with hydrogen under specific conditions.

Properties. They are volatile liquids. All are hydrolysed by water with the evolution of hydrogen, but the rates of hydrolysis differ greatly. Diborane has been studied more fully than others and most of the reactions of diborane may be considered as representative, although some differences do exist. Some of the important reactions of diborane are given below :



Structure of diboranes. These compounds are electron deficient because they do not contain as many electrons as are needed to form the desired number of covalent bonds. In the simplest compound, diborane, the number of electrons available are 12—1 six from two boron atoms and six from six hydrogen atoms. However, 14 electrons are needed to form 7 covalent bonds as in ethane. The recent investigations, based on infra-red and electron diffraction studies, have shown that diborane has a "bridge structure" in which each boron atom is bonded to two hydrogen atoms (known as "terminal hydrogen atoms") by regular electron pair bonds. The two boron atoms and four hydrogen atoms lie in the same plane, while the two bridging hydrogen atoms lie symmetrically one above and one below this plane. The structure is illustrated below.



The higher boranes are also electron deficient compounds and have similar hydrogen bridges. It will be of interest to know that Professor William N. Lipscomb was awarded 1976 Nobel prize for his work on boranes.

5.9. OCCURRENCE OF ALUMINIUM

Aluminium does not occur in free state. In combined state it occurs as : (i) **Oxides** : corundum, Al_2O_3 ; diaspore $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$; bauxite, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. (ii) **Fluoride** : cryolite, Na_3AlF_6 . (iii) **Silicates** : feldspar, KAlSi_3O_8 , mica, clays such as kaolin. (iv) **Basic sulphate** : alunite, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$.

The chief ore of commercial interest is *bauxite*, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, which contains about 55–60% Al_2O_3 . Its colour is dirty white (if it contains too much of silica, SiO_2) or red (if it contains too much of Fe_2O_3). In India, bauxite occurs in large quantities in M.P. Bihar, Bombay, Mysore, Tamil Nadu and Kashmir.

5.10. EXTRACTION OF ALUMINIUM

Production of aluminium from bauxite is carried out as follows :

Step I. Grinding and crushing. Big rocks of the bauxite are crushed in gyratory crushers and ground to fine powder in ball mills.

Step II. Purification of bauxite Bauxite usually contains large amount of impurities like SiO_2 , Fe_2O_3 . It is usually purified by either of the following methods.

(a) *Baeyers process* (suitable for red bauxite, i.e., containing much of Fe_2O_3). The finely powdered bauxite is heated with 40% NaOH solution at about 425K under 5-6 atmospheric pressure in an autoclave, when Al_2O_3 dissolves in solution as sodium meta aluminate.

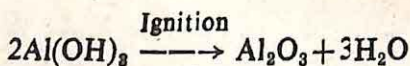


The impurities Fe_2O_3 , $\text{Fe}(\text{OH})_3$, SiO_2 , etc., remain undissolved and these are then filtered off.

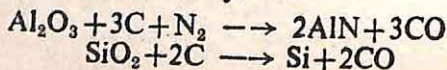
The filtrate containing sodium meta-aluminate is diluted with water and stirred vigorously at 350K with a little freshly precipitated $\text{Al}(\text{OH})_3$, which acts as a nuclei for precipitation of $\text{Al}(\text{OH})_3$ by hydrolysis.



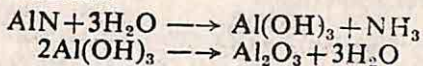
The precipitate is filtered, washed, dried and ignited to get pure alumina.



(b) *Serpeck's process* (suitable for white bauxite, i.e., containing much of SiO_2). Bauxite is heated with coke in a current of N_2 at 1275K, when AlN is produced ; whereas impurity SiO_2 is reduced to silicon which volatilizes away.



The AlN is then hydrolyzed with water to yield $\text{Al}(\text{OH})_3$, which is calcined to get pure alumina.



Step III. Reduction (Hall-Heroult's Process). Aluminium possesses the great affinity for oxygen and the reduction of Al_2O_3 by C is not possible under ordinary conditions. At high temperature, reduction takes place, but Al reacts with C to form Al_4C_3 . The reduction can be carried out electrolytically, but this too encounters the following difficulties.

- (i) Pure Al_2O_3 has very high melting point, 2275K.
- (ii) Al_2O_3 is a bad conductor of electricity.
- (iii) If electrolysis of fused alumina is carried out at 2275K, Al formed vaporises as its boiling point is about 2075K.

Hall-Heroult overcame these difficulties by mixing alumina with cryolite (Na_3AlF_6) and fluorspar (CaF_2) in the ratio 1 : 3 : 1, whereby the mixture becomes good conductor and it fuses at about 1175K.

The electrolysis is carried out in a cell consisting of an iron box lined inside with graphite, which serves as cathode. The anode is a set of carbon rods suspended in the electrolyte from copper clamps. The bottom of the cell is inclined towards a tapping hole.

To start with the anodes are lowered to touch the graphite lining at the bottom and current (100 amperes and 6-7 volts) is switched on. As the cell gets heated, cryolite is added. As the cryolite melts, the anodes are raised up to the middle of the cell.

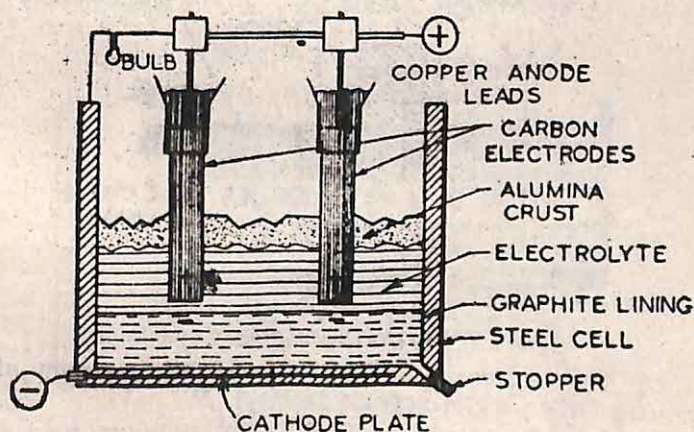
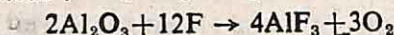
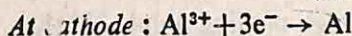
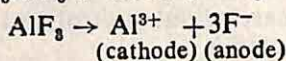
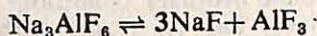


Fig. 5.1. Electrolysis of fused alumina.

Then, purified alumina is added so that its concentration in the electrolyte is about 20%. As soon as alumina is added, electrolysis starts forming Al and oxygen. The aluminium formed collects at the bottom of the cell (cathode) from where it is withdrawn from time to time from the tapping hole. The oxygen liberated attacks

the carbon anodes forming CO and CO₂. So, anodes have to be replaced after sometimes.

Due to electrolysis the concentration of alumina in the cell falls, and when it becomes less than 10 per cent a lamp connected in parallel glows and at this state more alumina is added so that process continues. Following reactions take place.



Step IV. Purification of aluminium (Hoope's process). Aluminium obtained as above is about 99 per cent pure. Further purification can be effected by Hoope's electrolytic process. In this the electrolytic cell consists of an iron tank lined at the bottom with carbon, which serves as anode. A number of graphite rods, suspended from above serves as cathode. The cell is filled with three liquid layers of different densities.

(i) The "topmost layer" consists of molten pure aluminium, which is in touch with cathode.

(ii) The "middle layer" is of electrolyte consisting of mixture of molten fluorides of Al, Ba and Na.

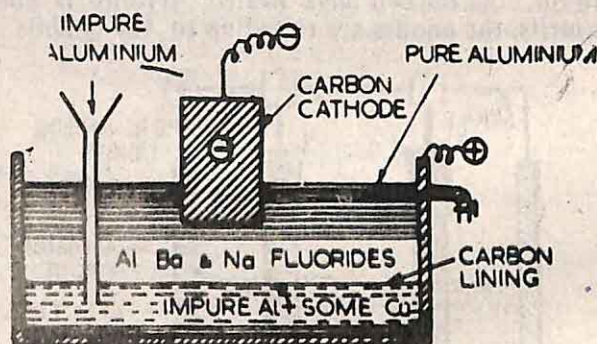


Fig. 5.2. Electrolytic refining of aluminium.

(iii) The "bottom layer" consists of molten impure aluminium containing some Cu (to increase density).

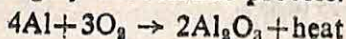
On passing electric current the aluminium ions from the middle layer are discharged at the cathode and collect in the topmost layer. Some amount of aluminium ions from the bottom layer goes into the middle layer. Pure aluminium collected at the top is tapped out from time to time. Crude or impure aluminium is added to the bottom layer from time to time. The process is thus continuous.

5.11. USES OF ALUMINIUM

(i) For preparing utensils, surgical instruments, parts of aeroplane, etc. (ii) For making overhead electric wires. (iii) Al foils for wrapping cigarettes, sweets and confectionery. (iv) In powder form for making silvery paints. (v) As a reducing agent in the production of Cr, Mn, etc. (vi) In thermite welding process. (vii) As a "dioxidiser" in the manufacture of steel. (viii) For winding the "moving coils" of dynamos and motors. (ix) As an absorber in the preparation of antibiotics (chloromycetin, streptomycin). (x) In powder form along with $\text{Al}(\text{NO}_3)_3$ in bombs. (xi) For making many useful alloys like duralumin, magnalium, aluminium, bronze, etc. (xii) In the extraction of Mg, Sr, etc. (xiii) In the manufacture of artificial rubber, perfumes, dyes and drugs. (xiv) As a dioxidiser in light alloys.

5.12. GOLDSCHMIDT'S THERMIT PROCESS

This was invented by Goldschmidt in 1905. The process is based on the principle that aluminium has a great affinity for oxygen and its oxidation is a highly exothermic process.



The enormous amount of heat produced melts the metal formed.



Temperatures as high as 3000K may be reached.

Thermit is mixture of 3 parts of ferric oxide and one part of aluminium powder. It is placed in a fire-clay crucible. The bottom of the crucible has a hole fitted with a tapping plug. It is placed

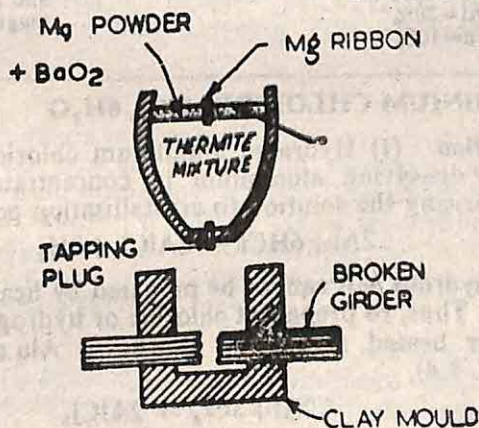


Fig. 5.3. Thermit welding.

just above the broken parts to be welded. Thermit mixture is covered with a mixture of aluminium powder and barium peroxide. This is called the *ignition mixture*. Magnesium ribbon is set in the ignition mixture. The ribbon is used as a starting fuse.

The broken ends of the parts to be welded are cleaned and placed as shown in Fig. 5.3. When the magnesium ribbon fuse is ignited, the ignition mixture catches fire and then the reduction of iron oxide by aluminium powder occurs. On removing the tapping plug, molten iron falls between the broken parts and join up. The excess or superfluous metal is then trimmed off. This process is used for welding big girders at site.

5.13. ALLOYS OF ALUMINIUM

The composition, properties and uses of some of the important alloys of aluminium are given in the Table 5.2.

Table 5.2. *Alloys of aluminium*

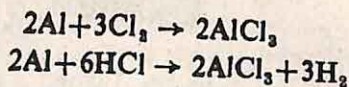
<i>Alloy</i>	<i>Composition</i>	<i>Properties</i>	<i>Uses</i>
Aluminium bronze	Cu=94.88% Al=5.12%	Golden colour, corrosion resistant.	For making utensils, jewellery, coins, etc.
Magnalium	Mg=5 to 15% Al=95 to 85%	Hard and tough.	In making parts of machine and cheap balances.
Nickeloy	Ni=1% Cu=4% Al=95	Very light and tough.	In making aircraft.
Duralumin	Al=95% Cu=4% Mg=0.5% Mn=0.5%	Light, hard, corrosion resistant and highly ductile.	In making aircrafts and seacrafts.
Alnico	Fe=50% Ni=20% Al=20% Cu=10%	Highly magnetic	In making powerful and permanent magnets.

5.14. ALUMINIUM CHLORIDE, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$

Preparation. (i) Hydrated aluminium chloride, $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, is obtained by dissolving aluminium in concentrated hydrochloric acid and vaporising the solution to crystallisation point.



(ii) Anhydrous salt cannot be prepared by heating the hydrated crystals. Thus, to prepare it chlorine or hydrogen chloride gas is passed over heated aluminium powder. Aluminium chloride sublimes (Fig. 5.4).



The vapours has the molecular formula, Al_2Cl_6 .

(iii) Commercially, anhydrous aluminium chloride is prepared by passing chlorine over a heated mixture of alumina and carbon.

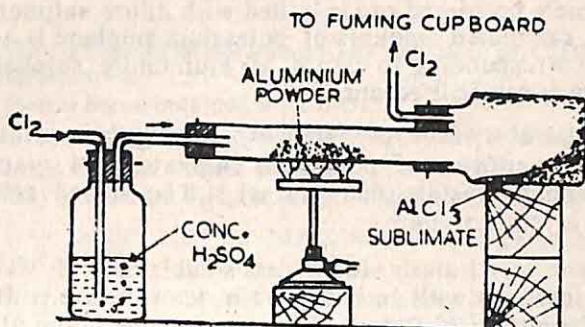
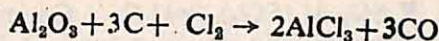
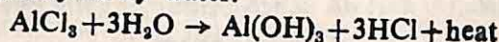


Fig. 5.4. Making of anhydrous aluminium chloride.

Properties. (i) It is a white crystalline deliquescent substance which fumes in moist air.

(ii) It is hydrolysed by water.



(iii) It absorbs ammonia to give $\text{AlCl}_3 \cdot 6\text{NH}_3$ and forms addition compounds with NO_2 , SO_2 , H_2S , etc.

(iv) When heated to 458K it sublimes. Below 623K its vapour density corresponds to the formula Al_2Cl_6 ; whereas above 1023K it corresponds to AlCl_3 . At ordinary temperatures its molecular formula is Al_2Cl_6 . Al_2Cl_6 molecules may be represented as shown in Fig. on page 2·59.

Uses. Anhydrous aluminium chloride is used (i) In petroleum refining and as a catalyst in Friedel—Craft's reaction and in cracking of gasoline. (ii) As mordant in dyeing. (iii) As medicine in locomotor ataxia.

5.15. ALUMS

In the beginning a double sulphate of potassium and aluminium was called alum but now all the double sulphates, composition of which may be written according to the formula $\text{R}_2\text{SO}_4 \cdot \text{M}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ are called alums. R stands for a monovalent metal e.g., Na, K, Rb, Cs, Ag, NH_4 , etc; and M stands for a trivalent metals e.g., Al, Fe and Cr, etc. All alums are soluble in water, are *isomorphous* and form octahedral crystals.

Alums may be prepared by adding the solution of corresponding metal sulphates in stoichiometric proportions and then concentrating to the crystallisation point. Out of these potassium aluminium alum is of special importance. It is also known as "*potash alum*" or just alum.

Potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. Commercially it is prepared from the mineral alunite or alumstone, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$. Finely powdered ore is boiled with dilute sulphuric acid. Subsequently, calculated amounts of potassium sulphate is added to the solution (corresponding to excess of aluminium sulphate) and from this alum is crystallised out.

In the laboratory it is prepared by mixing hot solutions of equimolecular quantities of potassium sulphate (174 grams) and aluminium sulphate crystals (666 grams). The mixed solution is cooled to get crystals of alum.

Properties. (i) Potash alum is less soluble in cold water, but the solubility increases with an increase in temperature. (ii) It is insoluble in alcohol. (iii) Potash alum melts at 396K and at 473°K loses all its water of crystallisation and turns to a porous mass. Anhydrous alum is known as "burnt alum."

Uses. (i) As a mordant. (ii) In tanning hides. (iii) For coagulating muddy water. (iv) For stopping bleeding of small wounds. (v) In fire extinguishers. (vi) In calico printing. (vii) For sizing paper.

QUESTIONS

(A) Essay Type :

1. Name the elements of group III A and give their electronic configuration. Discuss the general features of the group.
2. How does boron occur in nature? Write the formula of its chief mineral. Outline the extraction of boron from borax.
3. How does aluminium occur in nature? Name two important minerals of aluminium. How is it extracted from these minerals? Describe its important properties and uses.
4. How will you prepare the following substances from aluminium?
(i) anhydrous aluminium chloride; (ii) potash alum. Also list some uses of the two substances.
5. Write short notes on the following. (i) Goldschmidt's thermit welding; (ii) Alloys of aluminium metal; (iii) Uses of aluminium metal.
6. Give reasons only :
(i) an aqueous solution of aluminium chloride is electrically conducting, whereas fused aluminium chloride is not electrolysed.
(ii) aluminium is an active element, still nitric acid may be kept in aluminium containers;
(iii) on adding sodium carbonate solution to alum solution, aluminium hydroxide is precipitated instead of aluminium carbonate.

(B) Short-Answer Type :

7. Explain higher melting and boiling points of boron as compared to those of aluminium.
8. From the high ionisation energy of boron, will you expect its compounds (like BCl_3 , B_2H_6 , etc.) to be ionic or covalent?
9. While preparing aluminium why alumina is carefully purified?
10. For precipitating aluminium hydroxide, ammonium hydroxide solution is added and not sodium hydroxide solution. Give reasons.

11. For what alum is used by barbers and dyers ?
12. Why does strongly heated $\text{Al}(\text{OH})_3$ give an acid insoluble Al_2O_3 ?
13. Why is aluminium not obtained by reduction of Al_2O_3 with carbon at a high temperature ?
14. How is boron obtained from B_2O_3 ?
15. Draw the structures of BF_3 , BCl_3 , NH_3 , B_2H_6 and Al_2Cl_6 .
16. List some uses of boric acid.
17. Why is diborane (B_2H_6) an electron deficient compound ?
18. What is the chemical composition of the glassy bead formed on heating borax ?
19. Give equations involved in the borax bead test as applied to copper salts.

(C) Objective Type :

20. Put a tick mark for the correct answer :
 - (a) In aluminothermit process, aluminium is used as (i) an oxidising agent, (ii) a reducing agent, (iii) a flux, (iv) a solder.
 - (b) Which one of the following minerals does not contain aluminium ? (i) cryolite, (ii) felspar, (iii) clay, (iv) fluor spar.
 - (c) When metallic aluminium is treated with dilute or concentrated nitric acid (i) $\text{Al}(\text{NO}_3)_3$ is formed, (ii) NH_4NO_3 is formed, (iii) metal becomes inactive, (iv) H_2 gas is liberated.
 - (d) Which one of the following statements is false for boric acid ? It is used, (i) As a mild non-irritating ; (ii) in food preservation ; (iii) in pottery glazes and enamels ; (iv) to prepare baking powder.
 - (e) Aqueous solution of borax is (i) acidic, (ii) basic, (iii) neutral.

The Carbon Family- Group IVA Elements

		s-Block (Representative Elements)										p-Block (Representative Elements)									
		Groups																			
		IA																			
Periods	1	H																			
	2	Li Be																			
	3	Na Mg																			
	4	K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr																			
	5	Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe																			
	6	Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn																			
	7	Fr Ra Ac Ku Ha																			

6.1. GENERAL DISCUSSION

Group IV A of the periodic table consists of five elements, e.g., carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). They have a similar electronic configuration (ns^2, np^2), i.e., each has two electrons in the s -orbitals and two electrons in the p -orbital of the outermost shell. This attributes a common oxidation states of 4 to all these elements. The electrons in the p -orbitals go a long way to decide the combination of these elements with other elements. Hence, they are termed as p -block elements. Electronic configuration and some of the physical properties of this group are listed on next page.

6.2. GENERAL CHARACTERISTIC AND TREND

The elements carbon, silicon, germanium, tin and lead are typical in their behaviour showing a marked gradation in their properties. The similarity is rather less prominent and there is no such resemblance between C and Pb as we find between Li and Cs.

(1) **Electronic configuration.** All these elements have the same pattern of arrangement of electrons in their outer electronic

Table 6.1. Properties of elements of carbon family.

Property	C	Si	Ge	Sn	Pb
Electronic configuration	(He)2s ² , 2p ²	(Ne)3s ² , 3p ²	(Ar)3d ¹⁰ , 4s ² , 4p ²	(Kr)4d ¹⁰ , 5s ² , 5p ²	(Xe)4f ¹⁴ , 5d ¹⁰ , 6s ² , 6p ²
Abundance (ppm)	3.20 × 10 ³	2.772 × 10 ⁵	0.7 × 10 ¹	4.0 × 10 ¹	1.6 × 10 ¹
Atomic radius (Å)	0.77	1.11	1.22	1.41	1.47
Density (g cm ⁻³)	2.22 (graphite)	2.49	5.36	7.30	11.34
Melting point (K)	3853	1683	1210	505	600
Boiling point (K)	5100	2628	3103	2543	2013
First ionization energy (kJ mol ⁻¹)	1086	787	760	700	715
Electronegativity	2.50	1.74	2.00	1.70	1.55

shell, i.e., s², p². In the excited state, the atoms will have four bonding electrons :

	GROUND STATE		EXCITED STATE	
CARBON	2s ↑↑	2p ↑ ↑	2s ↑	2p ↑ ↑ ↑
SILICON	3s ↑↑	3p ↑ ↑	3s ↑	3p ↑ ↑ ↑
GERMANIUM	4s ↑↑	4p ↑ ↑	4s ↑	4p ↑ ↑ ↑

(2) **Non-metallic and metallic character.** The first two elements, carbon and silicon, are distinctly non-metallic. Germanium is "metalloid". Tin and lead are well-defined metals.

(3) There is marked gradation in atomic size and density. The values increase with the increase of atomic number.

(4) The melting and boiling points show the normal gradation with rising atomic number. The values decrease with increase of atomic number. The progressive lower melting points of germanium, tin and lead reflects the change from covalent bonding in carbon and silicon through germanium to metallic bonding in tin and lead. The same change is reflected in their crystal structures and their electrical conductance.

(5) **Ionisation energy and electronegativity.** All these elements are tetravalent. They possess high ionisation energies. Therefore, the existence of (4+) ions is unlikely. The electronegativity values are low (see Table 6.1), therefore (4-) ions also do not form normally. Thus, these elements prominently show a covalency of four, as a result of sp³ hybridisation of the orbitals. This also leads us to

understand the tetrahedral structures of the atom in case of carbon and its associates.

(6) **Allotropy.** All the elements, except lead, exhibit allotropy. Different allotropic forms of the same elements differ in physical properties. For example, of various allotropic forms of carbon, graphite and diamond are crystalline; while coal, coke, lampblack, charcoal, etc., are amorphous. Silicon also exists in crystalline and amorphous forms. White tin (ordinary crystalline) changes into grey tin (amorphous powder) at very low temperature.

(7) **Chemical behaviour.** This is perhaps the only sub group in which there is a steady increase in electropositive character with the rise of atomic number. Carbon and silicon are non-metals and tin and lead are metals; while germanium shows intermediate behaviour.

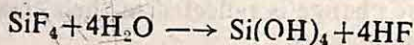
6.3. NATURE OF COMPOUNDS

(1) **Hydrides.** All form covalent hydrides, but with great differing ease. Thus, carbon forms enormous number of saturated and unsaturated hydrocarbons of ring and chain types (we will study about these hydrocarbons in details in part III—Silicon tend to form only a few such compounds (only saturated hydrides) named as hydrosilicons or silicoalkanes or silanes.

Silanes resemble the corresponding hydrocarbons in properties but are less stable. They are reducing agents and are easily hydrolysed by alkalis. Lower hydrocarbons and silanes on burning decompose to produce CO_2 and SiO_2 respectively along with water. Silane usually inflames on mere exposure to the air; whereas hydrocarbons burn only when lighted. Germanium forms only three hydrides, GeH_4 , Ge_2H_6 and Ge_3H_8 . Tin and lead form only one hydride (MH_4) each. The stability of the common hydride, MH_4 , decreases with increase in atomic number.

(2) **Halides.** The elements of groups IVA form tetrahalides, MX_4 . The carbon halides, such as CF_4 and CCl_4 , are the stablest and chemically inactive. They are not hydrolysed even by strong alkalis. Mixed chlorofluoro-hydrocarbons are known as "freons". They are unreactive and nontoxic and are widely used as "refrigeration fluids". The tetrahalides of the other elements Si, Ge, Sn and Pb are reactive. They have two chief characteristics.

(i) **Hydrolysis.** All these tetrahalides are hydrolysed by water. SiF_4 is readily hydrolysed to form orthosilicic acid, Si(OH)_4 .



GeCl_4 and GeBr_4 are hydrolysed less readily; while SnCl_4 and PbCl_4 are hydrolysed but the hydrolysis is incomplete, which is repressed by small amounts of acids.

(ii) **Complex formation.** In the presence of excess of acid, the halides of Si, Ge, Sn and Pb increase their coordination number

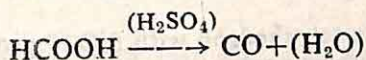
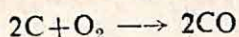
from 4 to 6 and form complex ions, such as $(\text{SiF}_6)^{2-}$, $(\text{GeF}_6)^{2-}$ and $(\text{SnF}_6)^{2-}$.



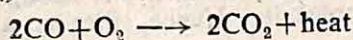
However, PbBr_4 and PbI_4 are not known.

(3) **Oxides.** The elements of Group IVA form two series of oxides-monoxide, MO and dioxides, MO_2 .

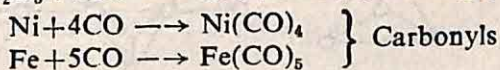
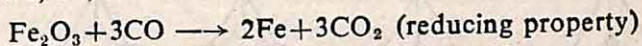
(i) *Oxides of carbon.* Carbon monoxide is formed by incomplete combustion of carbon in oxygen or air, or by dehydration of formic acid with concentrated H_2SO_4 .



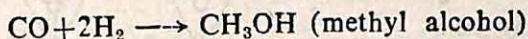
CO is a combustible gas which burns with pale blue flame.



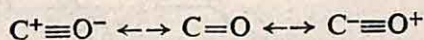
Carbon monoxide is good reducing agent and also forms carbonyls with metals like Fe , Ni , etc.



The catalysed reaction between CO and H_2 is used for the manufacture of methyl alcohol.



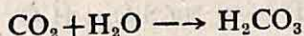
The electronic structure of CO is represented by resonance hybrid as ;



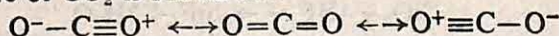
"Carbon dioxide" CO_2 , is formed by freely burning carbon in air or oxygen. It is acidic and reacts with alkalies to form carbonate, e.g.,



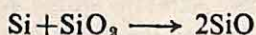
It is the anhydride of carbonic acid, H_2CO_3 .



The structure of CO_2 is shown as :

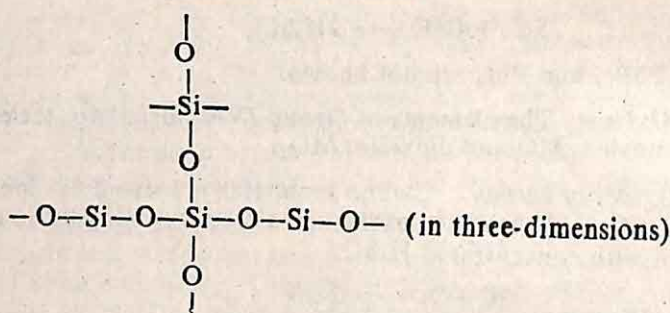


(ii) *Oxides of silicon.* SiO is supposed to be formed by heating silicon with silica, but its existence at ordinary temperature is doubted.



Silicon dioxide, commonly known as silica is formed by heating silicon with oxygen. Unlike CO_2 , SiO_2 does not exist in discrete

(unlinked) molecules. It consists of three-dimensional networks of linked silicon and oxygen as shown below :



The unit structure is a tetrahedron with SiO_4^{4-} group (Fig. 6.1) and in the structure as a whole each oxygen atom is common to the two tetrahedra (Fig. 6.2). The crystal lattice is strong and considerable energy is required to break it. Hence, silica is a solid with high melting point.

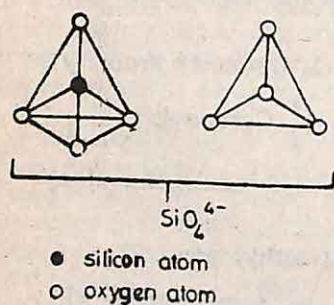


Fig. 6.1. Unit structure in silica.

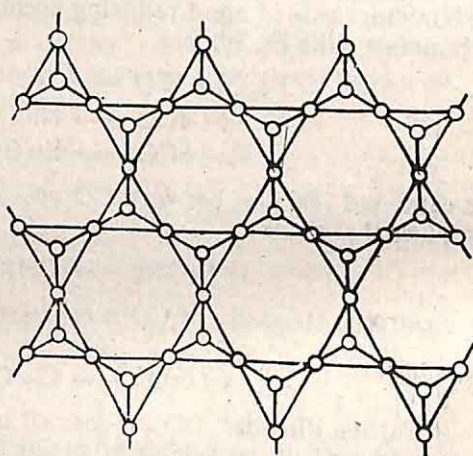
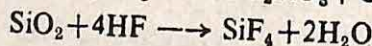
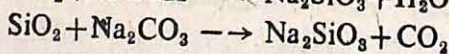


Fig. 6.2. Linkage between the tetrahedra.

Silica is generally unreactive. However, it reacts with fused alkalis to form silicates and with HF to form SiF_4 .



Silica exists in several forms, the three main crystalline forms are quartz, tridymite and cristobalite; quartz being the commonest. The amorphous variety of silica are chert, flint, chalcedony and jasper.

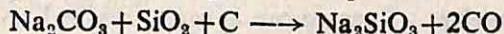
Uses. Silica is used in making glass and as building material (in mortar) and as abrasive. "Quartz" is used as refractory (silica bricks), in optical instruments for ultraviolet lamps. "Agate" is used in preparing hard knife-edges. "Rock-crystal" is used as gem

stone and for lenses. "Kieselguhr" is used as an adsorbent. "Silica gel" is used as a dehydrating agent and as a medium for the dispersal of finely divided catalysts and "fine amorphous silica" is used as filler for rubber goods.

(iii) *Oxides of Ge, Sn and Pb.* The more common dioxide GeO_2 , SnO_2 and PbO_2 decrease in acidity. Thus, GeO_2 is not strongly acidic as SiO_2 , while the rest two are amphoteric. All the three dioxides dissolve in alkalis to form salts, i.e., germanate $(\text{GeO}_3)^{2-}$, stannate $(\text{SnO}_3)^{2-}$ and plumbate $(\text{PbO}_3)^{2-}$. All the three oxides are insoluble in acids. However, with HF and concentrated HCl they form complex ions such as $(\text{GeF}_6)^{2-}$ and $(\text{SnCl}_6)^{2-}$. The monoxide, GeO , SnO and PbO , are more basic and ionic than dioxides. GeO is distinctly acid; while SnO and PbO are amphoteric.

(4) *Silicates.* Silicates are the salts of silicic acids. Many silicates corresponding to the numerous hypothetical complex silicic acids are found to occur in nature. Here we shall study some most important silicates.

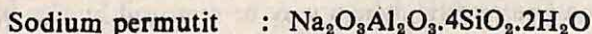
Sodium silicate. Na_2SiO_3 . It is prepared by fusing sodium carbonate with pure sand or powdered quartz and charcoal.



After the reaction is over, the mass is boiled with water under pressure in an autoclave. Sodium silicate dissolves in it and the unreacted sand and charcoal are filtered off. They filtrate in then concentrated by evaporation to a thick syrup of the density 1.3 and supplied to the market under the name *water glass* or *soluble glass*.

Uses. It is used (i) as a soap filler and to give soap a good finish; (ii) for making casts and artificial stone; (iii) as a binder in making abrasive wheel and in refractory linings of furnaces; (iv) for sizing walls and for making water-proofing materials; (v) for preserving eggs by sealing their shells with a layer of impervious silicate; (vi) for making silica gel; and (vii) for making a chemical garden.

Permutits. The double silicates of sodium or potassium with aluminium are known as "Zeolites". They largely occur in nature. When artificially made, these are called "permutits." The permutits are represented by chemical formula as follows:



Sodium permutit is prepared by fusing together sodium carbonate, sand, charcoal and china clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$). It is largely used for softening hard water. The fundamental unit from which silicates are derived is $(\text{SiO}_4)^{4-}$ complex, in which the silicon lies at the corners (c.f. Fig. 6.2). These complex ions are present as discrete units in the ortho silicates, but in more complex structure one, two or three oxygen atoms are common to two or more tetrahedra. The metallic ions in most cases are present in tetrahedral holes or in octahedral holes depending on their size.

6.4. OCCURRENCE OF TIN AND LEAD

The most important ore of tin is tinstone or cassiterite, which contains SnO_2 . The most abundant ore of lead is lead sulphide, galena, PbS and this is the principal source of commercial lead.

6.5. EXTRACTION OF TIN

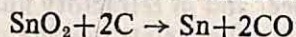
Tin is extracted from tinstone, SnO_2 , using the following steps.

(i) **Concentration.** The ore usually contains only 10 per cent SnO_2 . To increase its concentration, the ore is crushed in jaw crushers and then finely powdered in ball mills. Powdered ore is washed in running water so that the ore is freed from lighter impurities, e.g., clay, silica, etc. The tungstates of iron and manganese, which are present as impurities, are magnetic and hence they are removed by magnetic separation.

(ii) **Roasting.** The concentrated ore is then roasted in an inclined revolving furnace. In this process sulphur and arsenic, etc., are removed as volatile products and Cu, Fe are changed to oxides or sulphates.

(iii) **Washing.** Roasted ore is again washed in a stream of water to dissolve the soluble sulphates and to carry away lighter particles of ferric oxide and other impurities. Tin oxide, being heavy, easily settles down. The washed product contains about 70% SnO_2 and is called "black tin."

(iv) **Smelting.** Black tin is mixed with one-fifth its mass of anthracite coal and some lime (flux) and the mixture is smelted on the hearth of a reverberatory furnace at 1570K to 1760K. Tin oxide is reduced to metallic tin and carbon monoxide is given off.



Molten metal collects at the base of the furnace and the impurities present combine with lime to form a slag, which floats over the molten metal. Slag is removed with the help of perforated spoons and molten metal is drawn off from below and cast into blocks. The tin, thus, obtained is about 99.5% pure.

(v) **Refining.** Tin obtained above contains traces of iron, lead, tungsten and arsenic, which may be removed by the processes given below :

(a) **Liquidation.** Impure tin is melted on the sloping hearth of a reverberatory furnace when pure molten metal (m.pt. 505K) flows down leaving behind insoluble solid impurities.

(b) **Poling.** Molten metal is stirred with green logs in presence of air when the impurities rise to the surface and get oxidised to form a scum on the surface which is then removed.

(c) **Electrolytic refining.** It is refined further by an electrolytic process. A mixture of hydrofluosilicic acid, tin sulphate and

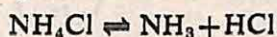
sulphuric acid is taken as the electrolyte. Anode is made of impure tin and cathode is made of pure thin tin plates.

Uses. It is used (i) for tin plating sheets of iron used for making food cans and oil containers, (ii) in tinning household utensils, (iii) for making alloys like bronze, solder, type metal, several easily fusible alloys and some dental alloys, (iv) for the preparation of tin compounds commonly used as mordants in dyeing and calico-printing. An amalgam of tin is used in making mirrors.

6.6. TINNING

Food stuffs usually contain a number of organic acids. When they are placed in utensils of copper, brass, etc., the acids react in presence of air to form soluble metal salts, which are poisonous. Kitchen utensils are coated with tin metal to prevent action of food acids.

Utensiles to be tinned are cleaned thoroughly by rubbing with sand or stone dust. Some ammonium chloride powder is sprinkled over the heated surface and the surface is rubbed with a pad of cotton. Hydrochloric acid liberated due to dissociation of NH_4Cl , removes any oxide film present on the surface.



A small amount of tin is melted on the hot surface and is uniformly spread all over with the help of cotton pad carrying some more ammonium chloride powder. The vessels after tinning must be cleaned before use, to remove salts formed during ammonium chloride treatment.

6.7. ALLOYS OF TIN AND LEAD

Important alloys of tin along with their composition, properties and uses are given below :

Name	Composition	Properties	Uses
Bronze	Cu=88 to 96% Sn=4 to 12%	Hard to wear ; takes a high polish, rather brittle.	In making utensils, statues and coins.
Bell metal	Cu=80% Sn=20%	Hard, produces melodious sound, rather brittle.	For making bells and gongs.
Solder	Sn=30 to 50% Pb=70-50%	low melting point.	For soldering.
Type metal	Pb=82% Sb=15% Sn=3%		Type for printing.

6.8. EXTRACTION OF LEAD

The extraction of lead is mostly done from *galena* as this is the most abundant of its ores. For high concentration ores, extraction is carried out by the self-reduction process; whereas for low concentration ores, extraction is carried by carbon-reduction process.

(1) Self-reduction process. This process involves the following steps.

(i) *Concentration*. The crushed and finely powdered ore is concentrated by froth floatation process.

(ii) (a) *Roasting*. Concentrated ore is roasted at moderate temperatures in a reverberatory furnace, lined inside with silica

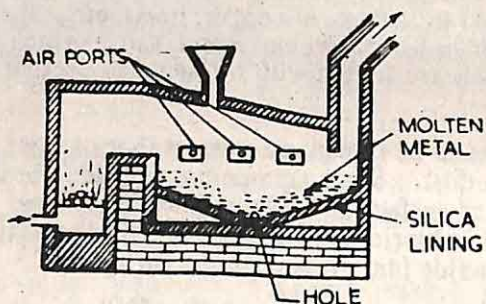
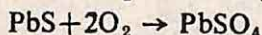
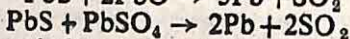
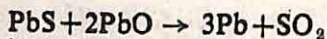


Fig. 6.3. Reverberatory furnace for lead extraction.

bricks, in a controlled supply of air (Fig. 6.3). By controlling the supply of air following reactions occur during roasting.



(b) *Smelting (Reduction of galena)*. At an appropriate stage of oxidation, air supply is cut off and after adding some more of galena and lime, the temperature of the furnace is raised when the oxide and the sulphate formed in the roasting step are reduced to metallic lead.



Molten metal slips to the bottom of the furnace. It is taken out from time to time. Lime reacts with the impurity of silica and forms a slag which floats over the molten lead.

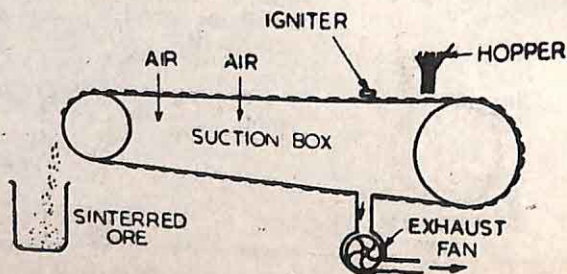
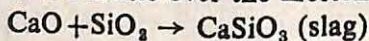


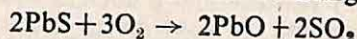
Fig. 6.4. Revolving belt roaster.

Thus, in this process roasting and smelting of the ore is completed in the same furnace at different temperatures.

2. Carbon-reduction process. It is completed in the following steps.

(i) *Concentration*. It is carried out by the froth floatation process.

(ii) *Roasting and sintering in a Dwight-Iloyd roaster*. Previously, sintering and roasting were done in a furnace similar to Bessemer converter, but now-a-days it is done on a revolving belt roaster (Fig. 6.4). In this machine a band moves on rollers. Finely powdered concentrated ore after mixing with coke and lime (flux) is charged on the moving band and is ignited at once. In the presence of air, the ore gets roasted as it moves on. The speed of the band is adjusted in such a way that the ore is completely roasted when it reaches the other end. Exhaust fans, fixed below the band, continuously draw air so that the required air is supplied for the roasting of the ore. The ore supplies the fuel also. The advantage of this process is that the ore is sintered while roasting goes on.

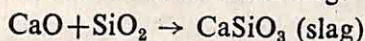


(iii) *Smelting*. Reduction of the roasted ore is done in a blast furnace. The roasted and sintered ore is mixed with coke and limestone and is smelted in a blast furnace. The furnace is 5 to 7 m in the height and about 2m in diameter and is water-jacketed (Fig. 6.5). The following reactions occur in this furnace,

(a) Coke reduces lead oxide to metallic lead.



(b) Lime reacts with silica to form slag.



(c) Any lead sulphate or silicate formed is changed to oxide by lime.

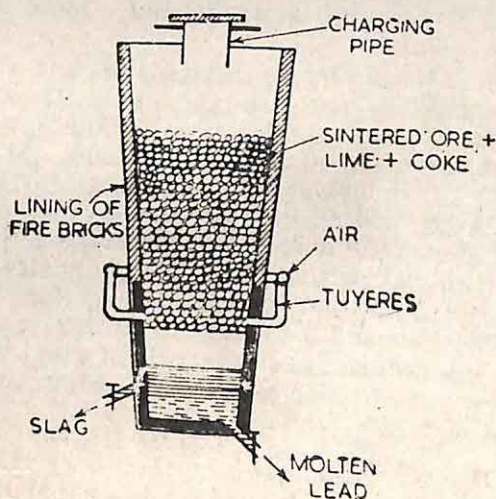
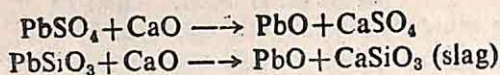
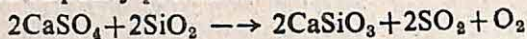


Fig. 6.5. Blast furnace for lead extraction.



The lead oxide is reduced subsequently.

(d) The calcium sulphate is also converted to silicate by the action of silica impurity present in the ore.

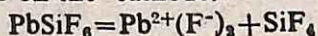


The molten metal and slag are taken out from separate holes at the bottom.

Refining. The lead obtained from either of the two processes contains copper, silver, iron, antimony, bismuth and zinc as impurities, which make the metal hard. When these impurities are removed, the metal becomes soft and the process is known as softening of lead. The impurities are removed by the following processes.

(i) *By oxidation.* Crude metal is melted on a shallow hearth of a reverberatory furnace and a current of air is passed through. The impurities present (except silver and gold) are oxidised and form a scum of oxides, which is removed. After this step silver and gold, if present, are extracted with molten zinc. Further refining is done by the electrolytic method.

(ii) *Electrolytic method.* This method was given by Bett. The impure lead is made the anode and very pure lead is used for cathodes. The electrolyte is lead fluosilicate (PbSiF_6). HCl and H_2SO_4 cannot be used as lead ions give precipitates with them. The presence of a small quantity of glue helps in the deposition of lead as a coherent layer on the cathode.



At anode : $\text{Pb} - 2\text{e}^- \longrightarrow \text{Pb}^{2+}$ (In solution)

At cathode : $\text{Pb}^{2+} + 2\text{e}^- \longrightarrow \text{Pb}$ (Deposited)

Gold and silver settles down as anode mud. More reactive metals are retained in solution.

Uses. Lead is used (i) for making pipes and sheets for chemical, industries underground cable coverings, outer coverings of telephone wire cores, (ii) for storing corrosive liquids, (iii) for making lead storage batteries, (iv) in making lead shots, (v) in filling marble engravings, (vi) in making lead pigments for paints such as white lead, litharge, red lead, chrome red ($\text{PbCrO}_4 \cdot \text{PbO}$) and chrome yellow (PbCrO_4), (vii) in making lead alloys, e.g., type metal, fusible alloys, (viii) in making solders of different grades, (ix) in making lead tetraethyl, (x) for making lead shields for radiation from radioactive substances and X-ray units. In this process lead does not change to any radioactive substance, but the lead used should be free from impurities which can become radioactive. Bismuth is one of such impurities.

6.9. COMPOUNDS OF LEAD

Lead forms two types of compounds—plumbous and plumbic. In plumbous compounds lead exists in a bivalent state and in

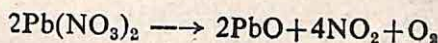
plumbic compounds it is in tetravalent state. Plumbous compounds are more stable. A few important compounds of both types are described below.

(1) **Plumbous oxide or lead monoxide, PbO.** Lead monoxide is found in two varieties—naturally occurring yellow variety is known as *massicot* and the other, somewhat reddish, a manufactured variety is known as *litharge*. These varieties are believed to differ in the size of their particles.

Preparation. (i) The yellow variety is obtained by passing a current of hot air or oxygen over heated lead (573K). On further heating it melts at about 1073K. When molten lead oxide is cooled a reddish variety is formed. Litharge is better known than massicot.

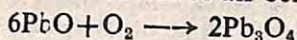


(ii) In the laboratory it may be prepared by heating lead nitrate.



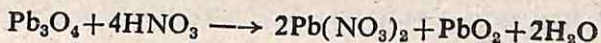
Uses. It is used (i) in glazing pottery, (ii) in making flint glass, (iii) in paint and varnishes, (iv) for joining broken glass pieces and stones and is an acid resisting cement, (v) in antiseptic ointment and in making lead plaster by heating linseed oil with litharge. It is a mixture of lead linoleate and glycerine.

(2) **Triplumbic-tetraoxide, Red lead, Pb₃O₄.** It is prepared by heating lead monoxide in excess of air below 825K.

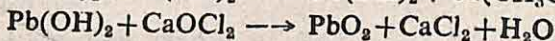


Uses. (i) For preparing red paint which is used for protecting iron and steel structures. (ii) In glass industry for providing PbO and oxygen. (iii) As an oxidising agent in the laboratory and in match industry.

(3) **Lead dioxide, PbO₂.** It is prepared by the action of nitric acid on red lead.



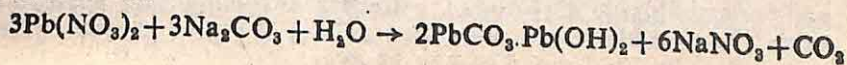
(ii) In laboratory it is prepared by the action of bleaching powder on any lead salt.



The first reaction occurs because of the presence of a small quantity of slaked lime in bleaching powder.

Uses. It is used as an oxidising agent in making lead storage batteries.

(4) **White lead, 2PbCO₃·Pb(OH)₂.** In the laboratory it is prepared by adding sodium carbonate solution to any soluble lead salt solution.



When basic lead carbonate is mixed to linseed oil, a very good white paint is formed. On a large scale it is prepared by the following two methods.

The Dutch Process. In this process perforated lead dishes (or buckles) are placed in earthen pots partly filled with dilute acetic acid (Fig. 6.6). These pots are placed on the floor, which is covered

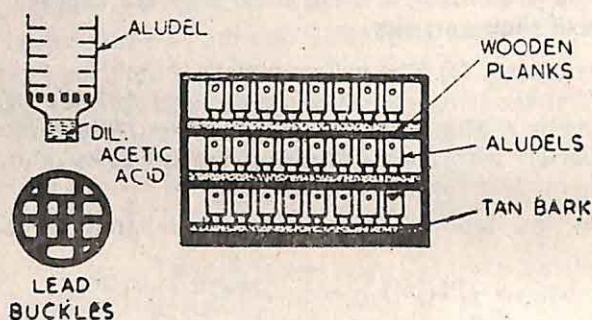
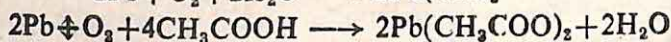
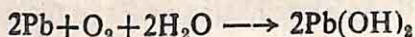


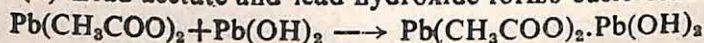
Fig. 6.6. Dutch Process of manufacturing white lead.

with a layer of spent tan bark or horse dung. The pots are covered with a wooden board, on which are placed more of spent bark and pots. Successive tiers of boards, bark and pots are placed one above the other, until the shed is full. The shed is then closed for 2 to 3 months. During the time, the tan bark undergoes fermentation. This gives heat and carbon dioxide, which bring about a slow conversion of lead into white lead. The possible reactions are :

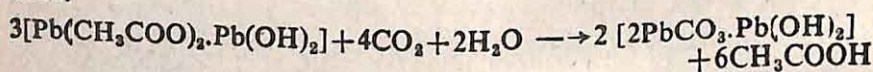
(i) In the presence of moisture and oxygen of the air and acetic acid vapour, basic lead acetate is formed.



(ii) Lead acetate and lead hydroxide forms basic lead acetate.



(iii) Basic lead acetate reacts with carbon dioxide to give white lead.



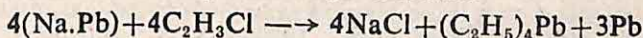
The acetic acid takes part in further conversion of lead to white lead.

After about three months the crust of white lead is stripped off. It is washed with water (to make it acetate free) and then finely ground.

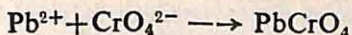
Carter's process. It is the modern method. In this method finely dispersed lead is obtained by blowing air through molten lead. These particles of lead are made to react with air, acetic acid, water and carbon dioxide in wooden cylinders revolving on horizontal axes. The possible reactions are the same as in Dutch process. However, white lead is formed in 5 to 12 days.

Uses. White lead is chiefly used for making white paints. It has greater covering power than any other white paint. The disadvantages of white lead are that it is tarnished by hydrogen sulphide present in the atmosphere due to formation of black (PbS) and is poisonous.

(5) **Tetraethyl lead.** It is added to petrol to decrease the trouble of knocking in the engine due to fuel. It is prepared by the action of sodium-lead alloy with ethyl chloride.



(6) **Chrome yellow, PbCrO_4 .** It is one of the least soluble salts of lead. It is precipitated when a soluble chromate is added to neutral or slightly acidic solution of lead salt.



This is used as pigment.

QUESTIONS

(A) *Essay Type :*

1. Name the elements of group IV A and give their electronic configurations. Discuss the general trends of group IV A elements.
2. Discuss, the general, the nature of compounds of group IV A elements with special reference to halides and oxides.
3. Give the preparation, properties and uses of carbon monoxide and carbon dioxide. Also discuss the nature of bonding and mode of hybridisation involved in their molecular structure.
4. What are silicate? How is sodium silicate prepared? List some uses of sodium silicate.
5. Name the chief mineral of tin and how is metal extracted from it? List some important uses of tin.
6. Describe carbon-reduction process for the extraction of lead from galena. List some important uses of the metal.
7. What are the oxides of lead? Give the industrial uses.
8. What is the formula of white lead? How is it prepared? Mention its important uses.
9. Give methods of preparation and uses of the following compounds. (i) lead tetraethyl, (ii) chrome yellow, (iii) red lead.
10. Give composition, properties and uses of the following alloys of tin and lead. (i) Bronze, (ii) bell metal, (iii) solder, (iv) type metal.

(B) *Short-Answer Type :*

11. What is the basic unit of silicates?
12. Write a short note on zeolites.
13. Name the different crystalline and non-crystalline variety of silica.
14. What is the formula of lead tetraethyl? Why is it mixed with petrol?
15. Write a short notes on "tinning."
16. Which is the compound of lead added to petrol as antiknock agent?

17. Separate the following into crystalline and non-crystalline form of silica.

(i) quartz, (ii) tridymite, (iii) cristobalite, (iv) chart, (v) flint, (vi) chacedony, (vii) jasper.

18. Mention at least one use each of bronze, bell metal and solder.

(C) Objective Type :

19. Put a tick mark for the correct answer.

(a) Water glass is the common name given to the chemical compound, known as (i) amorphous silica, (ii) kieselguhr, (iii) water soluble gas, (iv) sodium silicate.

(b) Silica is attacked by (i) concentrated HNO_3 , (ii) concentrated H_2SO_4 , (iii) hydrofluoric acid, (iv) aquaregia.

(c) Which one of the following statement is false for sodium silicate ? It is used (i) as a filler in soap industry, (ii) in calico printing, (iii) as antiseptic (iv) in the preservation of eggs.

(d) Which of the following compounds of elements in group IV A would you expect to be most ionic in character ? (i) PbCl_2 , (ii) PbCl_4 , (iii) CCl_4 , (iv) SiCl_4 .

(e) Alloys made of Bi, Pb, Sn and Cd melts (i) below 343 K, (ii) between 353 K to 363 K, (iii) between 363 to 373 K, (iv) above 373 K.

☐ ☐ ☐

The Nitrogen Family- Group VA Elements

s - Block (Representing Elements)																p - Block (Representing Elements)							
Periods	Groups	IA		d - Block Transition Elements										VIA					O				
	1	H	IIA											III A	IV A	VA	VIA	H	He				
	2	Li	Be											B	C	N	O	F	Ne				
	3	Na	Mg	III B	IV B	V B	VIB	VIB	VIII	IB	II B	Al	Si	P	S	Cl	Ar						
	4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
	5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
	6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
	7	Fr	Ra	Ac	Ku	Ha																	

7.1. GENERAL DESCRIPTION

Group VA of the periodic table consists of five elements, nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi). They possess an identical electronic configuration ns^2, np^3 , n being the last energy level in each case. The three electrons in the p -orbital attributes an oxidation number 3 to each of these elements. Since the p -orbital electrons govern the chemical behaviour of these elements, they belong to p -block elements. Some of the physical properties along with electronic configuration are listed in Table 7.1 on next page.

7.2. GENERAL CHARACTERISTICS AND TREND

(A) **Physical Properties.** (1) **Electronic configuration.** As given in Table 7.1, all the Group VA elements have 5 electrons in their outermost shell. Therefore, they exhibit a maximum valency of five. However, the tendency of the pair of s -electrons to remain inert increases with increase in atomic number. Therefore, these elements show valencies of 3 and 5 with halogens and sulphur. The hydrides are trivalent.

(2) **Atomic size.** The steady increase in size with increasing atomic number is apparent in this group (see Table 7.1). A comparison of the sizes of atoms in different oxidation state is of special

Table 7.1. Physical properties of nitrogen family.

Property	N	P	As	Sb	Br
Electronic configuration	(He) $2s^2, 2p^3$	(Ne) $3s^2, 3p^3$	(Ar) $3d^{10}, 4s^2, 4p^3$	(Kr) $4d^{10}, 5s^2, 5p^3$	(Xe) $5d^{10}, 6s^2, 6p^3$
Abundance (ppm)	3.0×10^2	1.2×10^3	0.3×10^1	0.1×10^1	0.02×10^1
Atomic radius (Å)	0.75	1.06	1.19	1.38	1.46
Ionic radius, M^{3-} (Å)	1.71	2.12	2.22	2.45	—
(in MO_3^-), M^{5+}	0.11	0.34	0.47	0.62	0.74
Ionisation energy (kJ mol ⁻¹), E_1	1403	1060	946	933	703
Density (g cm ⁻³)	0.96	1.82	5.72	6.69	9.80
Melting point (K)	63	317	1087 (36 atm.)	904	544
Boiling point (K)	77	553	Sublimes	1653	1933
Electronegativity	3.0	2.1	2.0	1.9	1.9

interest. The size of the radius for a particle in -3 oxidation state is very large and it is much smaller for $+5$ oxidation state. This is in accordance with the gradual increase in metallic character from top to bottom in the group.

(3) *Ionisation energy.* The ionisation energy of these elements are relatively high. The decreasing values of ionisation energy with atomic number in the group indicate that nitrogen holds its outer electrons most tightly; while bismuth holds least strongly. This is again in line with steady increase in the metallic character down the group.

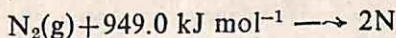
(4) *Electronegativity.* The electronegativity value of nitrogen is very high, 3, which shows its great affinity for electrons. The electronegativity values decrease with increasing atomic number thereby showing the increasing metallic character down the family to bismuth.

(5) *Metallic and boiling points and structural units.* The changes in melting and boiling points are not regular. This may be related to the fact that they exist in different structural units. Many of them (at least nitrogen, phosphorus and arsenic) exist as polyatomic molecules. The first member exists as diatomic (N_2) molecule. Phosphorus and arsenic forms P_4 and As_4 molecules. In the last two elements the metallic character predominates, and they crystallise as independent unit like metals.

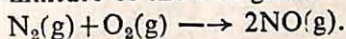
(6) *Allotropic forms.* Three elements (P, As and Sb) exhibit allotropy. In the solid state P, As and Sb have at least two allotropic modifications each; a non-metallic form of low density and

another a more density packed metallic form. Solid nitrogen has only a non-metallic structure; while solid bismuth has only a metallic one.

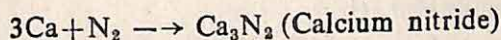
(B) **Chemical Properties.** (1) *Reactivity.* Nitrogen with an electronegativity of 3.0 is expected to be one of the most active elements, but it actually reacts with other elements only under extreme temperatures and pressures or in presence of catalysis. This is because a strong covalent bond, $\text{N}\equiv\text{N}$, exists between the two nitrogen atoms in the molecules of elemental nitrogen and the energy required to decompose such a molecule is very high.



Nitrogen combines with oxygen when a high voltage spark passes through a mixture of the two gases.



With very active metals, e.g., Ca, Mg, Li, etc., nitrogen reacts to form nitrides.



In contrast to nitrogen, phosphorus is very reactive. It burns readily in air forming trioxide (P_4O_6) and pentaoxide (P_4O_{10}) depending upon the availability of oxygen. Arsenic, antimony and bismuth are not affected by oxygen at ordinary temperatures. However, each burns to the trioxide. The elements of VA group, except nitrogen, combine directly with halogens forming either trihalides or the pentahalides. From the above description it is clear that the reactivity of these elements does not follow a regular trend. This is probably due to the variations in the structural unit.

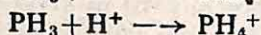
(2) *Oxidation states.* The common oxidation states of these elements are -3 , $+3$ and $+5$. This is in agreement with the number of electrons in the outer shell ($=5$). The tendency to lose three electrons and to be in -3 oxidation state is most pronounced in the case of nitrogen e.g. Mg_3N_2 , NH_3 etc., and it decreases with increasing atomic number until bismuth forms unstable compound, in which its oxidation state is -3 . The $+3$ oxidation state becomes progressively more important from phosphorus to bismuth (P_4O_6 , As_2O_3 , Sb_2O_3 and Bi_2O_3). Only Sb and Bi form simple cations in water solutions as do typical metals. These are Sb^{3+} and Bi^{3+} respectively. In tripositive state these materials can act as electron pair donors, but this property is pronounced only in case of nitrogen. In the $+5$ oxidation state these elements behave predominantly as non-metals, although the $+5$ oxidation state becomes less characteristic and more resistant to form as the atomic number increases.

7.3. NATURE OF COMPOUNDS

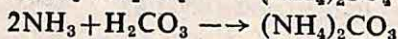
(1) *Hydrides.* "All" the elements of VA family form gaseous hydrides, MH_3 . They are all covalent and pyramidal in the shape. The properties of these hydrides change regularly as we descend in the group. Thermal stability decreases with rise of atomic number as indicated by their bond energies.

Bond	N—H ; P—H ; As—H ; Sb—H
Bond energy (kJ mol ⁻¹)	390.6 ; 319.2 ; 247.8 ; 256.2

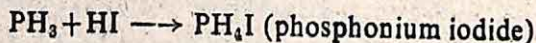
Bismuth hydride is so unstable that it may be obtained in small amounts only. All of these have a lone pair of electrons on the central atom which is utilized in interacting with acids, e.g.,



The ease with which the lone pair can be bonded to a proton ion (of the acid) decreases as we descend in the group. Accordingly, the basic character of the hydrides decreases down the group. Ammonia is distinctly basic and forms salts with both strong and weak acids.



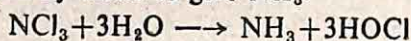
Phosphine (PH_3) is a weak base and forms salts only with strong acids like HI.



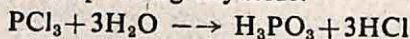
Arsine (AsH_3), stibine (SbH_3) and bismuthine (BiH_3) do not show basic properties at all and hence do not form any salt either with strong or weak acids.

(2) **Halides.** All the elements of VA family form halides. Trihalides of nitrogen (except NF_3) are very unstable and show an increase of metallic character with rise in atomic numbers. Thus, the b. pts. of trichlorides increase in the order NCl_3 (343K), PCl_3 (346.5K), AsCl_3 (403.2K), SbCl_3 (496K) and BiCl_3 (720K).

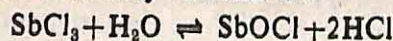
NF_3 is notable for its resistance to hydrolysis, but NCl_3 is readily decomposed by water to give NH_3 .



Hydrolysis of phosphorus and arsenic trihalides occurs with production of the corresponding oxyacids.



The trihalides of Sb and Bi (except BiF_3 which is definitely ionic) are hydrolysed reversibly as follows :



Pantahalides are formed by phosphorus and other heavier elements. PF_5 and PCl_5 are stable compounds. Nitrogen does not form pentahalides.

(3) **Oxides and Oxyacids.** All the elements of the nitrogen family form the trioxides, M_2O_3 , which are acidic in case of N, P and As ; amphoteric in case of Sb ; and basic in case of Bi. Thus, the acidic character goes on decreasing with increasing atomic number. The corresponding acids become less acidic and more basic. H_3BiO_3 has the properties of metal hydroxides, $\text{Bi}(\text{OH})_3$.

Almost all these elements form typical acidic pentoxides (M_2O_5). N_2O_5 is unstable and slowly decomposes even at ordinary temperatures. P_2O_5 is volatile but stable. The corresponding oxides of As, Sb and Bi are decomposed by heat into trioxide and oxygen. The acidic character of these oxides diminishes with increasing atomic number.

N_2O_5 gives only one monobasic acid (HNO_3) with water, P_2O_5 , on the other hand, gives a whole series of oxyacids like phosphorus acid (H_3PO_3), ortho phosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$) and metaphosphoric acid (HPO_3). Arsenic pentoxide forms the oxyacids, arsenous acid (H_3AsO_3) and arsenic acid (H_3AsO_4). Oxyacids of antimony and bismuth are not stable.

Nitrogen is, however, peculiar as it forms several oxides (N_2O , NO and N_2O_4) which have no counterparts in the other elements. Again N_2O_3 and N_2O_5 are monomeric; while P_4O_6 and P_4O_{10} are dimeric.

(4) **Sulphides.** *With the exception of nitrogen all the elements of the group form sulphides. The stability of the sulphides increases in descending the group. This is in conformity with the increase in electropositive character.*

7.4. AMMONIA

On a large scale ammonia gas may be prepared by any of the methods described below :

(1) **Synthetic process.** It is known as "*Haber's process*" and in it ammonia is prepared by a combination of nitrogen and hydrogen gas.

Principle. Nitrogen and hydrogen do not combine under ordinary conditions of temperature and pressure but in the presence of a catalyst and at appropriately high temperature and pressure they combine according to the following reversible reaction.



The forward reaction is exothermic also. We may use Le-Chatelier's principle, to work out the conditions of pressure and temperature for the maximum yield of ammonia.

Temperature. The reaction of the formation of ammonia is exothermic. Hence, low temperatures should be suitable for better yields at the equilibrium point. But at low temperatures the rate of formation will be very slow and it will take so long a waiting for the equilibrium to be reached that other costs of operation will increase and the process will not be commercially successful. Through experimental investigations it has been found that for practical purpose a catalyst has to be used and the process is operated at 700 to 750K. Above 750K the rate of reverse reaction increases and hence the yield of ammonia is decreased.

Pressure. In the formation of ammonia there occurs a decrease in volume (4 volume of reactant gases change to 2 volumes). Hence, according to Le-Chatelier's principle, increase of pressure will shift the equilibrium to a higher equilibrium concentration of ammonia. Within experimental limits of convenience, the pressure may be maintained between 200 to 1000 atmospheres.

Catalyst. Finely divided iron (with molybdenum or aluminium oxide used as a promoter) is found to be a good catalyst. It makes the approach to the equilibrium point closer and faster.

Between 700K to 750K temperature and at 200 atmospheric pressure, the yield is about 15% even when the equilibrium point is reached. In Claude's process, used in France, at the same temperature but by using a pressure of 900 atmospheres, the yield of ammonia can be increased to 40%.

Process. The plant used in Haber's process is shown in Fig. 7.1. The nitrogen (obtained by the fractional evaporation of liquid air) and hydrogen (obtained from water gas reaction or electrolysis of water) are mixed in the volume ratio of 1 : 3 and are pressed to a pressure of 200-900 atmospheres. The compressed gas mixture is passed over finely divided iron-molybdenum catalyst

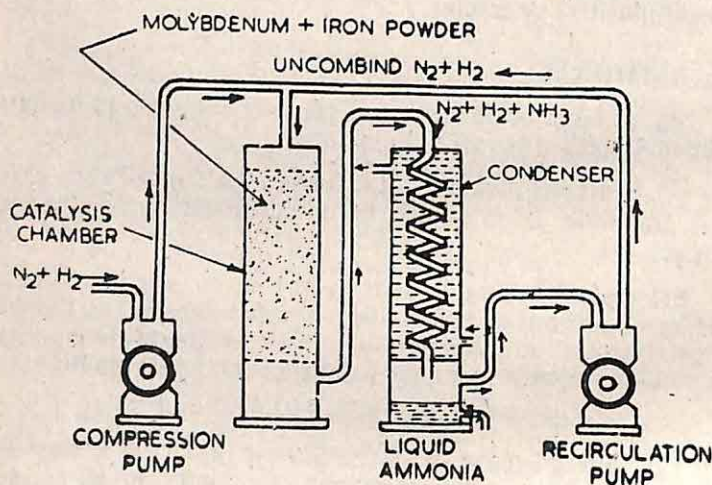
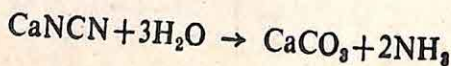


Fig. 7.1. Synthesis of ammonia by Haber's process.

heated electrically to 700-750K. The gas coming out from this chamber may contain 15 to 40 percent ammonia. Ammonia is recovered in liquid form by cooling. The unused gases are again sent back to the plant with the help of a recirculating pump.

(2) **Cyanamide process.** Calcium cyanamide is hydrolysed to produce ammonia when steam is passed over the cyanamide heated to 450K.



For preparing calcium cyanamide, nitrogen (obtained from liquid air) free from moisture and oxygen is passed over calcium carbide heated to about 1470K in an electric furnace,



Uses. (i) A large amount of ammonia is used as refrigerant in the manufacture of ice. For this purpose the gas is liquefied by increasing the pressure. The liquid ammonia thus obtained is passed through tubular coils (suspended in salt solution) by opening a stop-cock. It evaporates in the tubes (Fig 7.2). In this operation a large amount of heat is absorbed, which is taken from the salt solution in the tanks. In this way the temperature of the salt solution reaches below 0°C and the water placed in boxes is changed

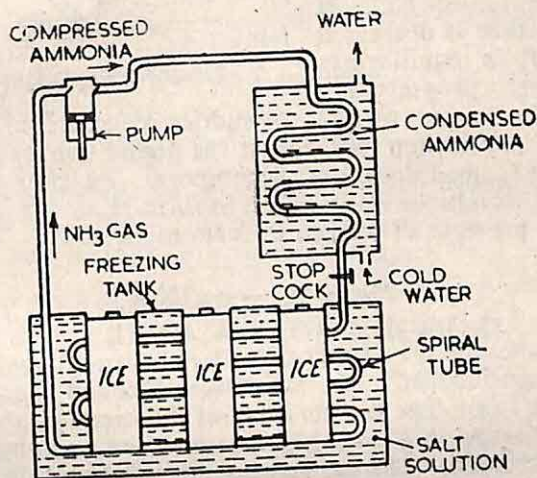


Fig. 7.2. Refregiration (schematic).

to ice. (ii) It is used in the manufacture of ammonium sulphate fertilizer, nitric acid (Ostwald process) and sodium carbonate (Solvay's process). (iii) It is used as a solvent in some reactions and as a cleaning agent for dissolving grease. (iv) In the laboratory it is used as a weak alkali. (v) It is used for manufacturing artificial silk.

7.5. NITRIC ACID

On a large scale it is prepared by the following two methods.

(1) From air (Birkeland and Eyde process). Nitrogen and oxygen combine to form nitric oxide.



The reaction is reversible and endothermic. According to Le-Chatelier's principle, use of high temperature will shift the equilibrium towards formation of more nitric oxide. The rate of formation of NO by this reactions becomes significant only at about 3200K. Increase of pressure has no effect on this equilibria as there is no change in volume of gases as reaction proceeds forward. Nitric oxide formed at high temperature has to be cooled very quickly down to 1270K to check the reverse reaction of decomposition of NO. If the temperature is decreased slowly a shift in equilibrium takes place progressively decreasing the amount of NO. A sudden decrease in temperature freezes the equilibrium position at the higher temperature and the NO gas once formed does not decompose. At room temperature nitric oxide combines with oxygen to form NO_2 . It is dissolved in water in the presence of oxygen to form nitric acid.

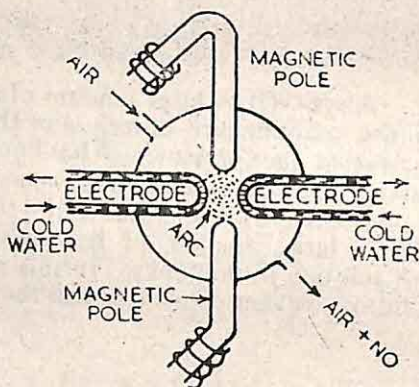
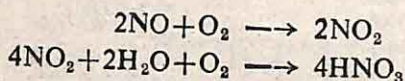


Fig. 7.3. Electric arc furnace.



Process. Purified air is passed through an electric arc furnace (Fig. 7.4). The temperature of the electric arc furnace is about 3300K. At high temperature nitrogen and oxygen combine to form nitric oxide. The gas coming out of the furnace contains about one percent nitric oxide. It is at once passed on to a cooling chamber where it is cooled to 1270K (Fig. 7.4). Steam raised, in boilers, is used for running the pumps.

Further on, the gases enter the oxidation chamber, where nitric oxide is oxidised to nitrogen peroxide.

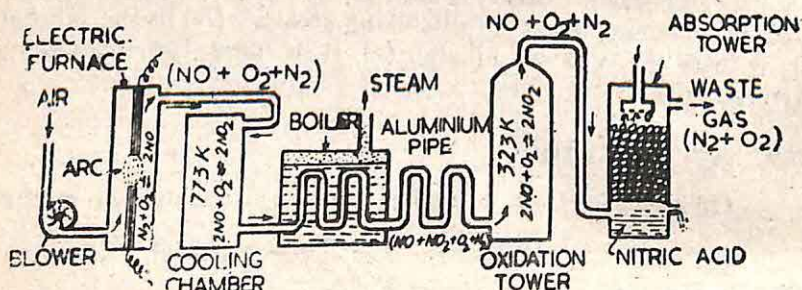
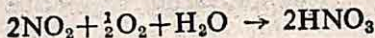
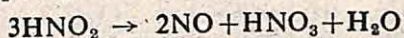
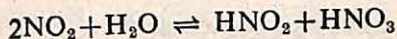


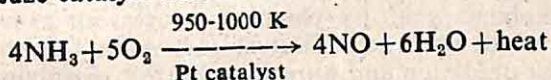
Fig. 7.4. Manufacture of nitric acid by Birkland-Eyde process.

The nitrogen peroxide thus produced is changed to nitric acid by water and more oxygen in the absorption tower.

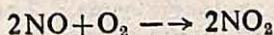


Birkland-Eyde process was earlier set up in Norway for manufacturing nitric acid, but this method has almost been now replaced by Ostwald's process, since the latter is less expensive and more convenient.

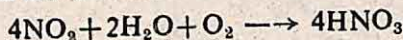
(2) From ammonia (Ostwald process). This is now the most important process for the manufacture of nitric acid. In this process ammonia is oxidised by an excess of air to nitric oxide in presence of platinum gauze catalyst heated to 950-1000 K.



Nitric oxide is cooled and combined with oxygen to form nitrogen peroxide.



The nitrogen peroxide in turn is dissolved in water in presence of air to form nitric acid.



Process. The plant used is shown in Fig. 7.5. Mixture of NH_3 gas and dust-free air in the volume ratio of 1 : 9 is passed through platinum gauze kept at 950-1000K. Ammonia is changed to nitric oxide by the catalytic oxidation. The heating is required in the beginning only ; heat evolved during reaction maintains the required temperature. The gases (nitric oxide, nitrogen and water vapour) coming out from the catalyst chamber are cooled to about 450-550 K and further mixed with more air and then passed on to the oxidation chamber where nitrogen peroxide is formed.

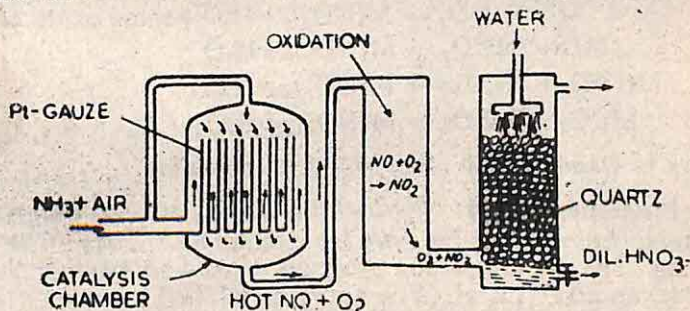


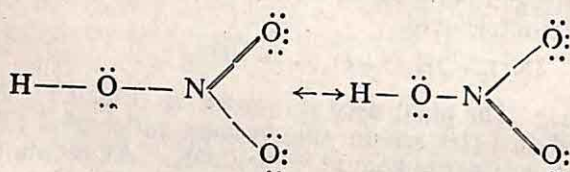
Fig. 7.5. Manufacture of nitric acid by Ostwald process.

The nitrogen peroxide thus produced is reacted with water in presence of oxygen where nitric acid is produced. The reaction is

carried out in an absorption tower which is packed with small pieces of quartz. Water tickles from the top.

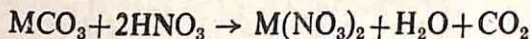
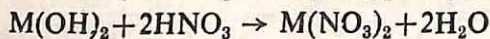
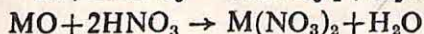
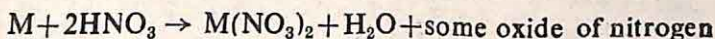
Uses : The main use of nitric acid is (i) In the production of explosives like trinitro-toluene (T.N.T.), trinitro-cellulose (gun cotton), trinitro-glycerine, dynamite (trinitroglycerine and kieselsol), a form of hydrated silica) and smokeless powder. Ammonium nitrate is used in explosives and fertilizers. Picric acid (ortrinitro-phenol) is also used in explosive mixture. (ii) In the production of the fertilizers, calcium ammonium nitrate (CAN). (iii) In the preparation of nitrates of metals. These are used in photography, pyrotechny and calico printing. (iv) For preparation of nitro compounds which are further used for making dyes, perfumes and medicines. (v) For the purification of gold and silver. (vi) In the preparation of some powerful galvanic cells. (vii) As aqua-regia for dissolving some metal alloys and minerals. (viii) In manufacture of sulphuric acid by chamber process for providing oxides of nitrogen, which work as a catalyst. (ix) As an important laboratory reagent for oxidation and nitration and for dissolving precipitates. (x) As a constituent of rocket propellants.

Structure of nitric acid molecule. The molecular structure may be represented by the two resonating structures.



7.6. NITRATES

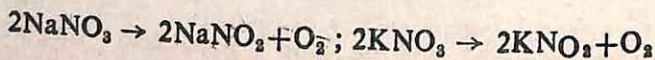
The salts of nitric acid are called nitrates. These are prepared by the action of nitric acid on metals, their oxides, hydroxides or carbonates.



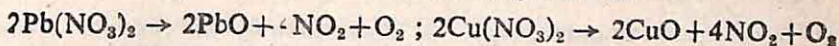
where M stands for an atom of a divalent metal.

Properties. *Almost all nitrates of metals are crystalline solids and are soluble in water. They are ionic in nature. They decompose on heating. The decomposition products depend on whether the nitrate is of (i) an alkali metal, (ii) a heavy metal, (iii) a noble metal, or (iv) ammonia. The decompositions of these nitrates are given below :*

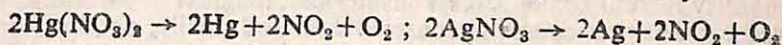
(i) *Nitrates of alkali metals liberate oxygen and leave behind a nitrite.*



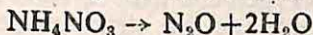
(ii) The nitrates of heavy metals liberate nitrogen peroxide in addition to oxygen and the metal oxide is left behind.



(iii) The nitrates of noble metals also liberate nitrogen peroxide in addition to oxygen but leave behind residue of metal itself.



(iv) Ammonium nitrate gives nitrous oxide on heating.



Ring test for nitrates. To an aqueous solution of nitrate, cold and concentrated sulphuric acid is added. Now a freshly prepared aqueous solution of ferrous sulphate is poured slowly from the side of the test tube. At the junction, where the two solutions meet, a brown ring is formed (Fig. 7.6).

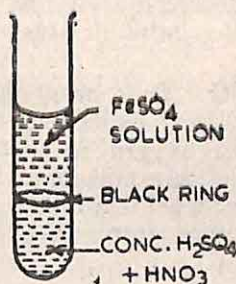
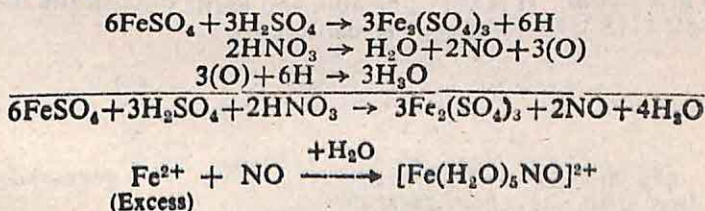


Fig. 7.6. Ring test for nitrate.

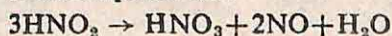
The ring is seen because of the formation of nitroso ferrous ion $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$. The reaction occurs as :



7.7. NITROUS ACID, HNO_2

This acid exists only in solutions and till now it has not been obtained in pure state in any physical form. Its salts, nitrites are however, well known. From them an idea about its structure and properties has been taken.

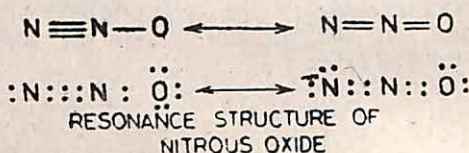
An ice cold and very dilute solution of the acid is stable. Even at room temperature it decomposes as :



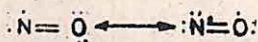
It is an oxidising as well as reducing agent. It is used in the manufacture of azo dyes.

7.8. OXIDES OF NITROGEN

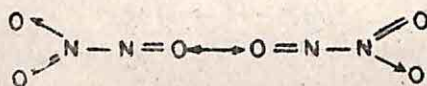
(1) Nitrous oxide, N_2O . It is prepared by the thermal decomposition of ammonium nitrate at 440-530K. Nitrous oxide is a colourless gas with a sweet taste and odour. When inhaled in small quantity nitrous oxide causes hysterical laughter. On inhaling a larger quantity it causes unconsciousness and finally, death. It is the least reactive amongst the oxides of nitrogen. At about 870K it decomposes to give oxygen and then it acts as an oxidising agent. N_2O is a linear molecule and the structure may be represented by the following resonance structures :



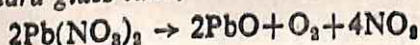
(2) Nitric oxide, NO . It is prepared by heating copper with 50% cold nitric acid. Nitrous oxide is a colourless poisonous gas. It readily combines with oxygen to give brown nitrogen dioxide (NO_2). It acts as an oxidising and reducing agent. It is used in the manufacture of nitric acid, and mixed with carbon disulphide to be used in flash light photography. Its resonance structures are :



(3) Dinitrogen trioxide, N_2O_3 . It is obtained by cooling an equimolecular mixture of nitric oxide and nitrogen dioxide at 253K as a blue liquid. It is very unstable and exists only in the solid state (m. pt. 171K). Its resonance structures are :



(4) Nitrogen dioxide or peroxide, NO_2 . It is prepared by heating lead nitrate in a hard glass tube.



Nitrogen dioxide is a reddish brown gas with a pungent characteristic odour. Effect of temperature on it may be represented as given below :



It is mixed hydride of nitrous and nitric acids. It is used in rockets as a source of oxygen.

(5) Nitrogen pentoxide, N_2O_5 . It is prepared by distilling concentrated nitric acid with phosphorus pentoxide at a low temperature.

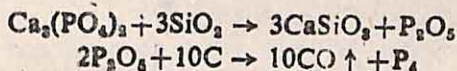


Nitrogen pentoxide is a colourless crystalline solid. As it decomposes readily to give oxygen, it acts as a powerful oxidising agent. It destroys almost all the organic compounds. After a recent study it is believed to be nitronium nitrate ($NO_2^+ - NO_3^-$) instead of a covalent nitrogen pentoxide.

7.9. PHOSPHORUS

Phosphorus is very reactive element ; hence it does not occur free in nature. In combined state it is widely spread as phosphates in several minerals. Important minerals are : phosphorite, $Ca_3(PO_4)_2$; fluorapatite, $3Ca_3(PO_4)_2 \cdot CaF_2$; and chlorapatite, $Ca_3(PO_4)_2 \cdot CaCl_2$.

Extraction of phosphorus. Now-a-days it is prepared by electric process. In this method phosphorus is obtained by directly heating mineral phosphorite with silica and coke.



The above reaction occurs above 1500K. The electric furnace used is shown in Fig. 15.7. The charge is fed continuously through

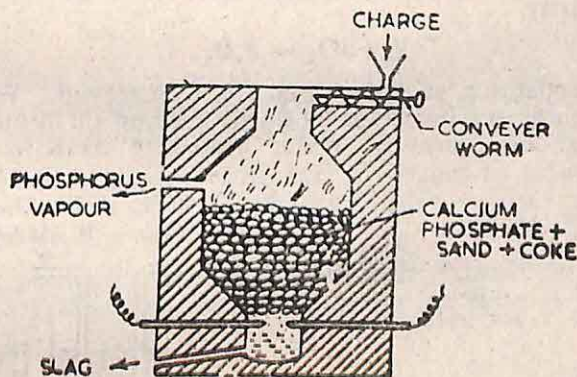


Fig. 7.7. Extraction of phosphorus.

a hopper. Molten calcium silicate is removed as a slag from the lower opening. The vapour of phosphorus is led under water for condensation as white phosphorus.

Uses of phosphorus. (i) In the manufacture of phosphor bronze—an alloy of Cu, Sn and P. (ii) It is used for incendiary bombs and smoke screens. (iii) In match industry and as a poison for rats and other pests.

7.10. OXIDES OF PHOSPHORUS

In the solid state phosphorus is made up of tetrahedral P_4 units. On reacting with controlled amount of oxygen, an oxygen atom takes a place on each of the six P—P bonds thereby forming P_4O_6 molecule. With excess of oxygen, an additional atom of oxygen links to each of the phosphorus atoms using the lone pair on it. This gives P_4O_{10} molecule. These steps are shown in Fig. 7.8.

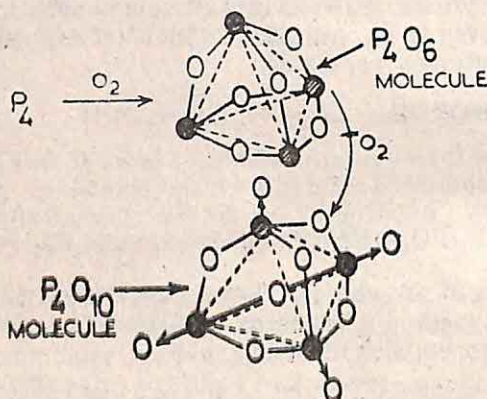


Fig. 7.8. Phosphorus and its oxides.

(1) Phosphorus trioxide or Tetraphosphorus hexaoxide, P_4O_6 . It is prepared by burning white phosphorus in a restricted supply of air. A small part of phosphorus pentoxide (P_4O_{10}) is also formed as an impurity.



The apparatus shown in Fig. 7.9 is employed. White phosphorus is burnt in a bent tube by slowly sucking air through it with the help of an aspirator. Water heated to 333K is circulated

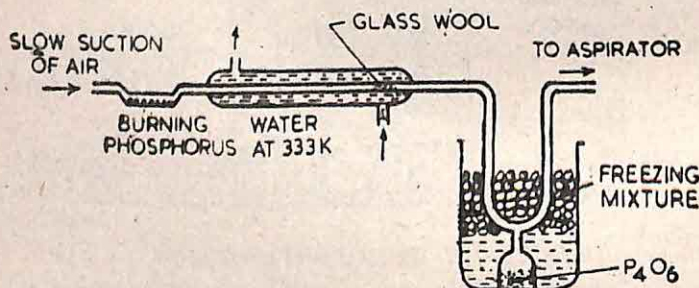


Fig. 7.9. Preparation of phosphorus trioxide.

through the Leibig condenser. Phosphorus pentoxide (formed along with the trioxide), being solid at 333K, is checked by the glass wool packing; vapour of the trioxide passes through and freezes to a solid mass in a U-tube placed in the freezing mixture.

Uses. It is used in the preparation of phosphorus acid.

(2) **Phosphorus pentoxide, P_4O_{10} .** It is prepared by burning phosphorus in presence of excess of dry air or oxygen.

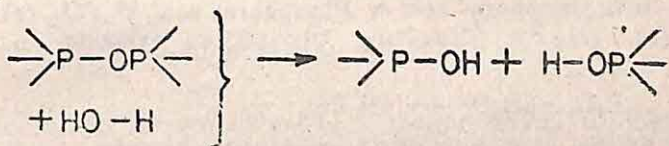


The sublimate of phosphorus pentoxide is obtained as a white crystalline solid.

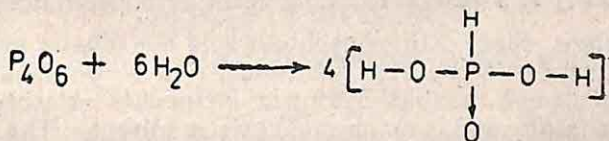
Uses. (i) As a strong dehydrating agent. (ii) For making phosphorus acid.

7.11. OXY-ACIDS OF PHOSPHORUS

The two main oxides of phosphorus P_4O_6 and P_4O_{10} have P—O—P bonds. When these oxides react with water, the H—OH bond and the P—OP bonds break to form two new bonds.



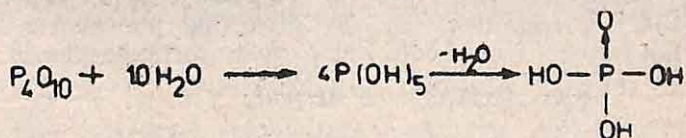
Thus, P_4O_6 on reaction with water gives $P(OH)_3$ (phosphorus acid).



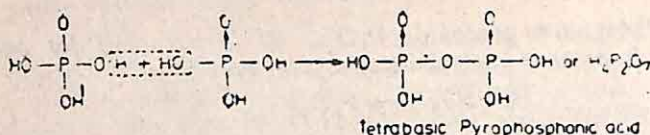
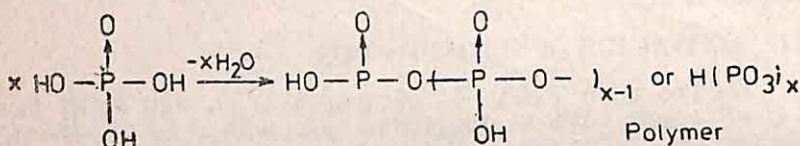
In ionising solvents the O—H bond breaks. The electronegative oxygen retains the electron pair. The P—H bond remains unaffected. Thus, phosphorus acid acts as a dibasic acid only.

The P—H bond can readily take up oxygen to get converted to P—OH bond. This behaviour is responsible for the phosphorus acid being a strong reducing agent.

P_4O_{10} react with water to produce $P(OH)_5$. $P(OH)_5$ is unstable and is stabilized by losing a molecule of water to $PO(OH)_3$ or H_3PO_4 .



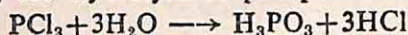
Dehydration of ortho phosphoric acid gives condensed acids.

(a) *Mild dehydration.*(c) *Drastic dehydration.*

(1) Orthophosphorus acid or Phosphorus acid, H_3PO_3 , $(\text{HO})_3\text{P}$.
Preparation. (i) By dissolving phosphorus trioxide in cold water.

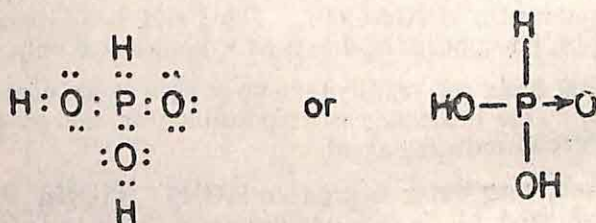


(ii) By the hydrolysis of phosphorus-trichloride.

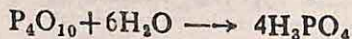


Uses. (i) In the preparation of organic and inorganic phosphites, and (ii) as a general reducing agent in the laboratory.

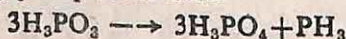
Structure. Since orthophosphorus acid is a dibasic acid, it is concluded that two OH groups are attached to the phosphorus atom in the molecule and the third hydrogen is directly attached to the phosphorus atom and is unionizable by the solvent. The structure assigned to H_3PO_3 molecule is:



(2) Orthophosphoric acid or Phosphoric acid, H_3PO_4 , or $(\text{HO})_3\text{P}=\text{O}$. **Preparation.** (i) By dissolving phosphorus pentoxide in hot water. Use of cold water gives metaphosphoric acid.

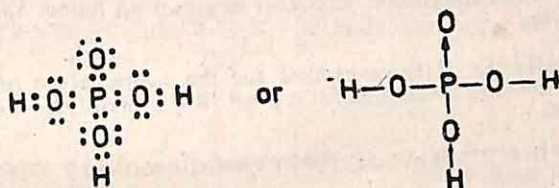


(ii) By heating phosphorus acid.



Uses. (i) In the manufacture of phosphorus element, and different inorganic and organic phosphates and phosphatic manures like triple super phosphate. (ii) In the preparation of hydrobromic acid from bromides. Phosphoric acid is non-volatile and does not possess any oxidising character (contrast sulphuric acid). (iii) In medicines to meet the deficiency of phosphorus in diet for stimulating secretion of gastric juice. This stimulates appetite and improves digestion.

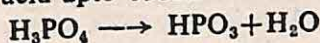
Structure. Being a tribasic acid, its structure may be written as :



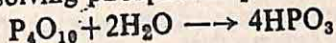
ORTHOPHOSPHORIC ACID (H_3PO_4)

Accordingly there are three OH groups linked to the phosphorus atom.

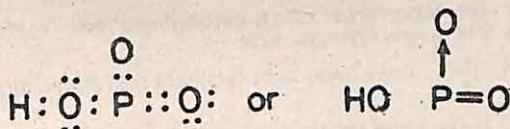
(3) **Metaphosphoric acid HPO_3 or $(\text{HPO}_3)_x$.** *Preparation.* (i) By heating phosphoric acid upto 593K .



(ii) By dissolving phosphorus pentoxide in cold water.



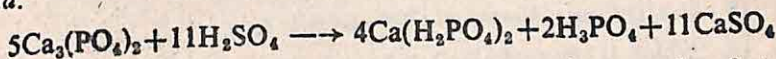
Structure. In solution it behaves as a monobasic solid and its structure may be represented as :



The acid and its salts tend to polymerise. Sodium hexametaphosphate, $\text{Na}_6(\text{PO}_3)_6$, is used in water softening and in detergents.

7.12. CALCIUM DIHYDROGEN PHOSPHATE, $\text{Ca}(\text{H}_2\text{PO}_4)_2$.

It is prepared by treating calcium phosphate with 70% sulphuric acid.



The product mixture is sold under the name of *superphosphate of lime*. It is an important fertilizer. The CaSO_4 formed in the above reaction has no use in agriculture and in recent year it has been eliminated by treatment of calcium phosphate with concentrated

ortho-phosphoric acid. This produces the desired phosphate only and thus formation of calcium sulphate is eliminated.



The product is known as *triple super phosphate*.

QUESTIONS

(A) Essay Type:

1. Name the elements of Group VA. Discuss the general features of group VA elements.
2. Justify the statement 'Elements of group VA follow the gradation in their properties.'
3. Describe the Haber's process for the manufacture of ammonia. What are the conditions favourable for a good yield? Mention some important uses of ammonia.
4. How is nitric acid prepared by synthetic method? Give a flow diagram of the unit used.
5. Describe the manufacture of nitric acid by Ostwald's process. Give the resonance structure of nitric acid.
6. What happens when the following compounds are heated?
(i) Ammonium nitrate, (ii) lead nitrate, (iii) silver nitrate, (iv) potassium nitrate.
7. Outline the chemistry of 'brown ring test' for nitrates.
8. Show that all the oxidation states from +1 to +5 are manifested in the oxides of nitrogen. How is nitric oxide prepared? Give its structure.
9. How is N_2O obtained? Give its resonance structures.
10. How is nitrogen dioxide prepared? What is the effect of heat on it? Give its most important use in modern days.
11. Write a short note on oxides of phosphorus.
12. Write a detail account of oxy-acids of phosphorus.
13. Draw the structures of (i) orthophosphoric acid, (ii) pyrophosphoric acid, (iii) trimetaphosphoric acid.
14. Name the most important fertilizer of phosphorus. How is it prepared?
15. Which is the chief source of phosphorus? How is the element obtained from it? Mention some important uses of phosphorus.

(B) Short Answer Type:

16. Name the elements belonging to ns^2, np^3 configuration. What are the various oxidation states which they exhibit?
17. State and explain 'inert pair effect' as applied to the elements of VA group?
18. Explain the existence of Sb^{3+} and Bi^{3+} ions.
19. Which is the acid obtained when P_4O_6 reacts with water?
20. What happens when phosphorus is burnt in excess of air?
21. Which are the acids obtained when P_4O_{10} reacts with water?
22. PCl_5 is known but not NCl_5 . Why?

(C. Objective Type :

23. Put a tick mark for the correct answer.

(a) Oxidation number of nitrogen in Mg_3N_2 is (i) 5, (ii) 3, (iii) -1, (iv) -3.

(b) Calcium cyanamide reacts with water to give (i) NO, (ii) N_2 , (iii) H_2 , (iv) NH_3 .

(c) An element which is usually found in explosives is (i) S, (iii) N_2 , (iii) Al, (iv) C.

(d) Laughing gas is (i) N_2O , (ii) NO, (iii) N_2O_4 , (iv) N_2O_5 .

(e) An hydride of nitrogen which is acidic (i) H_3N , (ii) H_4N_2 , (iii) H_2N_2 , (iv) NH_3 .

(f) Phosphoric anhydride is : (i) P_2O_3 , (ii) P_2O_5 , (iii) P_4O_{10} , (iv) P_4O_6 .

Introduction to Organic Compounds (Hydrocarbons)

1.1. A BRIEF HISTORICAL SURVEY

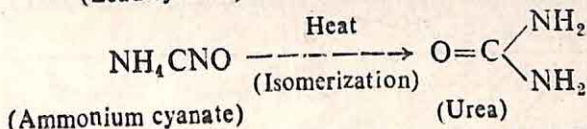
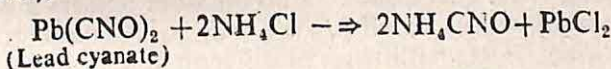
Pre-historic people were acquainted with substances like oils, fats, gums, starch, sugars, etc. ; also they were familiar with fermentation technique (*i.e.*, conversion of sugar and other sweet juices into wine). The art of preparing soaps from vegetable oils and fats, dyeing fabrics with indigo, madder roots (alizarin) goes back many centuries. *All these substances derived directly or indirectly from living organism, plants and animal sources were termed as "organic" so as to distinguish these substances from substances of mineral origin such as common salt, alums, blue and green vitriols, etc.*

Further study of the so-called organic substances revealed the fact that carbon is their essential constituent, since on burning in air (or oxygen) they always produced carbon dioxide.

1.2. VITAL FORCE THEORY

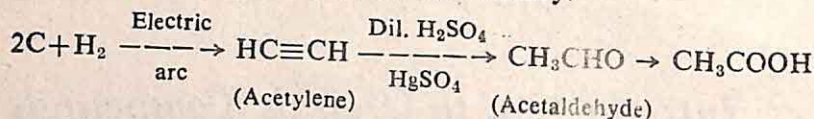
How these complex substances were being formed in the living plants or animals was explained by Berzelius, a leading Swedish chemist, on the assumption that *organic substances were being synthesized in the body of plants and animals under the influence of life or vital force present in the body of the living organisms. He also postulated that it is impossible to synthesize organic compounds artificially in the laboratory. This is known as Vital Force Theory.*

In 1828, F. Wholer, a German chemist, accidentally got urea (a typical organic compound in the urine of man and other mammals) by evaporation of ammonium cyanate, an inorganic compound composed of the inorganic constituents ammonia (NH_3) and cyanic acid (HCNO).



This synthesis gave a death blow to the 'Vital Force theory' and clearly demonstrated that no mysterious force was necessary

for the formation of organic substances. This theory met a lingering death as more synthetic compounds were added to the list of the organic compounds. A more convincing synthesis of acetic acid by Kolbe (1845) from inorganic substances proved to be the last nail driven into the coffin of the Vital Force Theory.



Thousands of organic compounds, formerly known as plant or animal products, have been synthesized without the least intervention of "Vital Force."

1.3. DEFINITION OF ORGANIC CHEMISTRY

The demarcation between organic and inorganic chemistry, though purely arbitrary, yet still retained since element carbon is found to be essential constituent of all organic substances. *Organic Chemistry today is the chemistry of carbon compounds*; while inorganic chemistry is that of all other elements and compounds. Although it is usual and conventional to include such common carbon compounds as carbon dioxide, carbon monoxide, carbonates and bicarbonates in the latter case. Retention of organic chemistry as a separate branch is a matter of practical convenience rather than any fundamental difference.

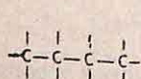
1.4. DISTINCTIVE FEATURES OF ORGANIC CHEMISTRY

The following are some of the observable points worth retrospective glance, which entails distinctive features of organic compounds.

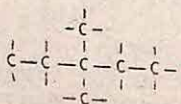
(1) **Vast number of carbon compounds.** The first thing that impresses us is the enormous profusion of organic compounds. The number of organic compounds so far discovered amounts to about ninety percent of the total number of known compounds. More than one million carbon compounds have been described and prepared and the number is increasing day by day.

(2) **Fewer number of constituent elements.** Another striking fact is that, although there are a large number of organic compounds yet they are composed of relatively few elements mainly carbon, hydrogen, oxygen, nitrogen, sulphur, halogens and less frequently phosphorus and metals.

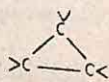
(3) **Long-chain compounds.** Carbon atom possesses a peculiar capacity to combine with itself to yield long chain compounds; open as well as closed, latter with rings of different shapes and sizes, e.g.,



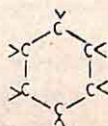
OPEN CHAIN



BRANCHED CHAIN



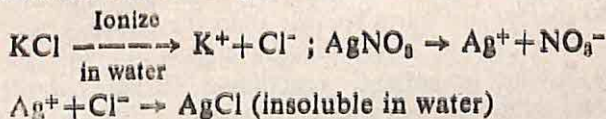
RING COMPOUNDS



(4) **Homologous series.** Organic compounds fall naturally into well defined groups of chemically similar substances having a general formula, forming an arithmatic series with a common difference of $-CH_2$. These series are called homologous series, which constitute a distinctive feature of organic chemistry. A homologous series have a characteristic group, general methods of preparation and general properties. Their physical properties usually show gradation. Thus, study of a vast number of organic compounds is reduced to the study of a comparatively fewer number of homologous series.

(5) **High molecular mass.** Organic compounds usually have a high molecular mass.

(6) **Non-ionic character.** Unlike the inorganic compounds, organic ones are mostly covalent and hence are non-ionic (i.e., do not ionize in water). In the case of inorganic substances the reactions are ionic in general. For example, if silver nitrate be added to a solution of potassium chloride, a white precipitate of AgCl is produced due to the presence of chloride ions.



However, chloroform (CHCl_3) or carbon tetrachloride (CCl_4) yields no precipitate with AgNO_3 even though containing high percentage of chlorine.

(7) **Low speed of organic reactions.** In general most of the organic reactions proceed very slowly in comparison to inorganic ones.

(8) **Low yield in organic reactions.** The yield of organic reactions is rarely theoretical which may be due to balanced or side reactions or both. Hence, organic reactions are more complicated than inorganic ones.

(9) **Non-applicability of the law of multiple proportions.** Apparent applicability of the law of multiple proportions does not seem to be valid to many of organic compound such as $\text{C}_{31}\text{H}_{64}$, $\text{C}_{60}\text{H}_{102}$, etc., which suggests a modification in the statement of the law to "when two elements combine to yield two or more different compounds, the mass of one which combines with a definite mass of the other in series of compounds bear an integral ratio, which may not necessarily be simple."

(10) **Comparative instability.** Unlike inorganic, organic ones do not show resistance to decomposition at high temperatures and as rule undergo decomposition at a red heat.

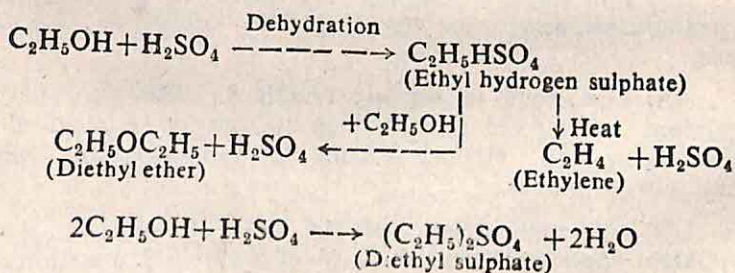
(11) **Isomerism.** Carbon compounds exhibit a peculiar phenomenon of isomerism. Substances possessing same molecular formula yet very different in properties are termed "isomers." This phenomenon is attributable to difference in arrangement of the constituent atoms. Thus, the formula $\text{C}_2\text{H}_6\text{O}$ stands for both ethyl alcohol

(C_2H_5OH) and dimethyl ether (CH_3OCH_3) which differ markedly in properties. Such isomerism effects are of limited occurrence among inorganic compounds. Thus, K_2SO_4 stands for only one substance potassium sulphate and nothing else.

(12) **Solvent.** In general substances having similar constitution are miscible in one another. Thus, fatty acids ($RCO-OH$), alcohols ($R-OH$), sugars are soluble in water ($H-OH$), since all of them contain hydroxyl grouping ($-OH$). Also for the same reasons most of carbon compounds are soluble in organic solvents like benzene, ether, chloroform, alcohol, petroleum, carbon disulphide, etc.; whereas inorganic compounds are mostly insoluble in them. Conversely, organic substances are much less soluble in water than inorganic ones.

(13) **Low melting and boiling points.** Organic compounds possess comparatively low melting and boiling points than inorganic ones. Also former are more volatile than the latter.

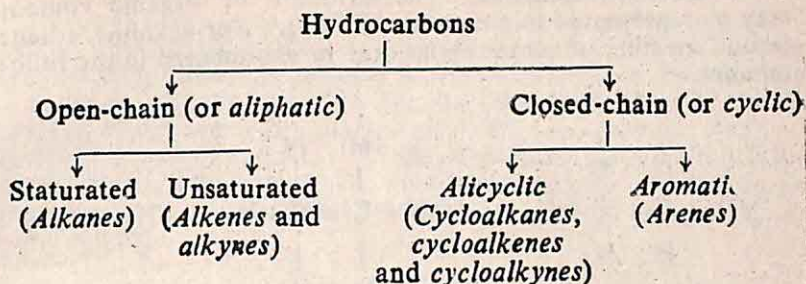
(14) **Factors in organic reactions.** Factors like temperature, pressure and concentration play an important role in organic reactions. For example, ethyl alcohol and sulphuric acid react together under different conditions to yield four different products—ethyl hydrogen sulphate, ethylene, ether and diethyl sulphate as indicated below.



(15) **Inflammability.** Organic compounds are mostly inflammable and there are only a few of them (like westron) which are not combustible (*i.e.*, they do not catch fire easily).

1.5. HYDROCARBONS AND THEIR CLASSIFICATION

The simplest organic compounds are made of hydrogen and carbon elements. On the basis of their elemental composition, they are called hydrocarbons. As electronegativities of hydrogen and carbon elements are nearly the same, these compounds are neither called hydrides nor hydrogen carbides. Hydrocarbons may be considered as the parent organic compounds from which other organic compounds are derived by replacement of one or more hydrogen atoms by other atoms or group of atoms. They may be classified as.



Hydrocarbons are broadly divided into two classes known as open-chain and closed-chain compounds. *Open-chain compounds* have been further classified into *alkanes*, *alkenes* and *alkynes* depending upon the presence of single, double and triple bonds between carbon atoms. *Alkanes, alkenes and alkynes are collectively known as aliphatic hydrocarbons.* Likewise, closed-chain compounds have been classified in *cycloalkanes*, *cycloalkenes*, *cycloalkynes* and *arenes* depending upon the presence of single, double and triple bonds between carbon atoms. *Cycloalkanes, cycloalkenes and cycloalkynes are collectively known as alicyclic hydrocarbons; where as arenes are known as aromatic hydrocarbons.*

8.6. ALKANES

Acyclic alkanes are the compounds of carbon and hydrogen in which all the valencies of carbon atoms are saturated with hydrogen atoms except those which are utilised in C-C linkage. In saturated hydrocarbons, combining powers of carbon atoms are fully utilised and therefore they do not form any addition compounds. *As they have a general lack of chemical activeness, they are given a group name of "paraffins"* (From Greek, *parum* means 'lack of' or 'low' and *affinis* means 'activity'). Paraffins form a homologous series which is given the general formula C_nH_{2n+2} . Examples of first ten members of alkanes with their common names are given below :

Molecular formula	Structural formula (condensed)	Common name
CH_4	CH_4	Methane
C_2H_6	CH_3-CH_3	Ethane
C_3H_8	$CH_3-CH_2-CH_3$	Propane
C_4H_{10}	$CH_3-(CH_2)_2-CH_3$	Butane
C_5H_{12}	$CH_3-(CH_2)_3-CH_3$	Pentane
C_6H_{14}	$CH_3-(CH_2)_4-CH_3$	Hexane
C_7H_{16}	$CH_3-(CH_2)_5-CH_3$	Heptane
C_8H_{18}	$CH_3-(CH_2)_6-CH_3$	Octane
C_9H_{20}	$CH_3-(CH_2)_7-CH_3$	Nonane
$C_{10}H_{22}$	$CH_3-(CH_2)_8-CH_3$	Decane

Structural formulae. The structure of organic compounds may be represented in a number of ways. For example, ethane the second member of alkane series may be represented in the following manner.

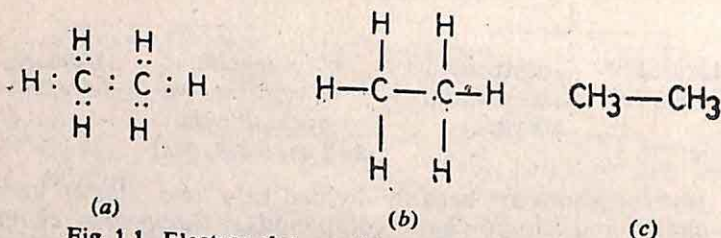


Fig. 1.1 Electron dot, graphic, rational formula of ethane.

In chapter IV (Part I) we have studied that the four valencies of carbon are directed towards the four corners of regular tetrahedron in space (formed by the hybridisation of sp^3 orbital) so the structural formulae (a), (b) and (c) do not show the actual positions of atoms in space. Spatial formulae shown in Fig. 1.2 (a), however, indicate the actual tetrahedral disposition of bonds. The bond above the plane of the paper is indicated by the heavy solid line, those below by dotted lines, while the one in plane is shown by ordinary line. Fig. 1.2 (b) represents the ball and stick model of methane. Similarly, Fig. 1.3 (a) and (b) represent two models of ethane molecule.

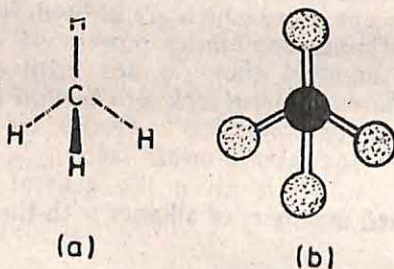


Fig. 1.2 (a) Spatial formula of methane.

(b) Ball and stick model for methane.

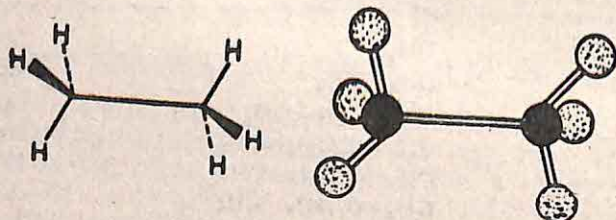


Fig. 1.3 (a) Spatial formula of ethane.

(b) Ball and stick model of ethane.

Conformation of ethane. The concept of conformation tells us about the relative positions of the atoms in a spatial model of a

molecule in gaseous or liquid state. In an ethane molecule the two methyl groups should be capable of free rotation about the C—C axis and thus should lead to numerous conformations. Studies have revealed, however, that only a few of these are possible. In the most stable conformation (having the least energy), the six hydrogen atoms are as far apart as possible, *i.e.*, they are staggered (see Fig. 1.4 (a), (b) and (c)). On the other hand, in the conformation of least stability (having the maximum energy) the six hydrogen atoms overlap. This is termed *eclipsed conformation* (see Fig. 1.5 (a) (b) and (c)).

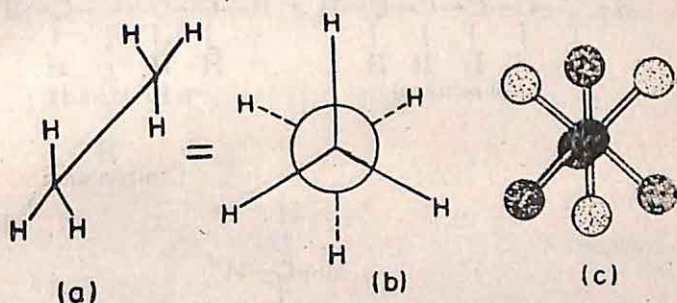


Fig. 1.4. Staggered conformation of ethane.

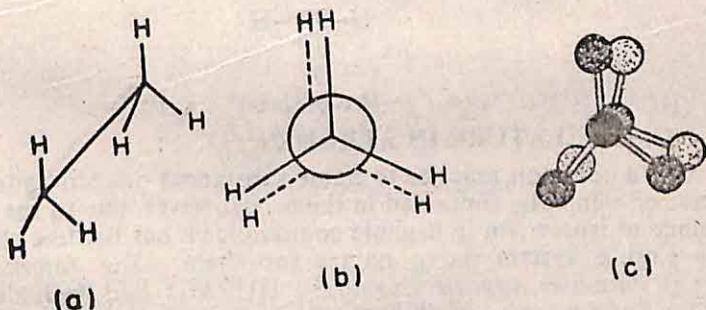
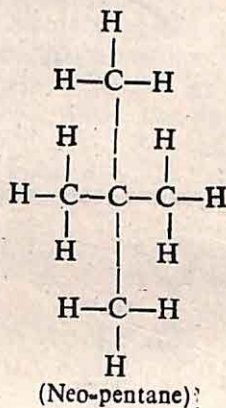
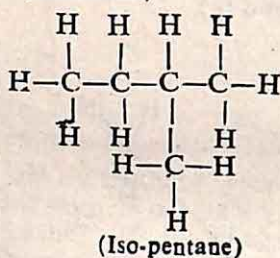
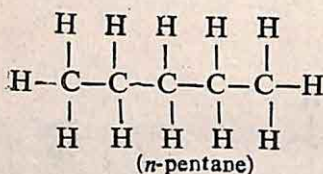
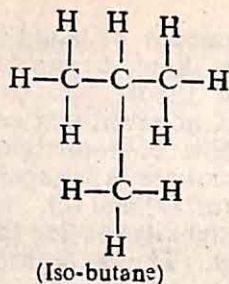
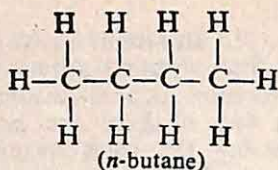


Fig. 1.5. Eclipsed conformation of ethane.

1.7. ISOMERISM IN ALKANE

Alkanes show only chain isomerism (i.e., having different chain structures for linking carbon atoms in case of members containing more than three carbon atoms. There are two butanes, three pentanes, five hexanes and so on. The number of isomeric molecules increase rapidly with an increase in the number of carbon atoms in the molecule. Common names of isomers of butane and pentane are given on page 3.8.



1.8. NOMENCLATURE IN ALKANES

It is a common practice to name substances according to their sources, or elements, contained in them. However, due to the heavy incidence of isomerism in organic compounds it has become essential to develop a system fixing names for them. The *International Union of Pure and Applied Chemistry* (IUPAC) had provided the steps for finding names of alkanes which are summarized below.

(1) In a hydrocarbon, first determine the longest continuous chain of carbon atoms and then the name of the hydrocarbon corresponding to this chain serves as the basis for naming it. It may be pointed out here that the selection of the longest chain does not depend upon how the formula is written.

(2) The selected longest carbon chain in them numbered, beginning at the end nearest the branching, so that lowest number can be given to the substituent (or group) present in the chain.

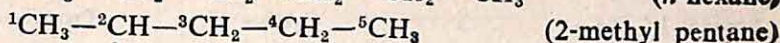
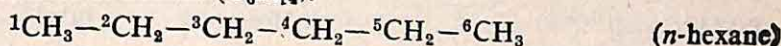
(3) In order to specify the position of the substituents other than hydrogens, they are given names as well as numbers. The name of

the side chain is obtained from the paraffin hydrocarbon by changing the ending—ane to—yl. For example, the side groups $-\text{CH}_3$, $-\text{CH}_2-\text{CH}_3$ are named methyl, ethyl, respectively.

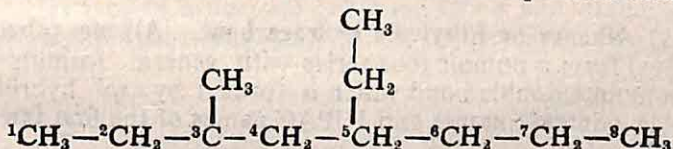
(4) When the carbon chain carries two like groups the number of location is repeated using prefixes di—, tri—, tetra—, etc.

(5) While writing the final name, place the name of the substituents in alphabetical order i.e., ethyl before methyl.

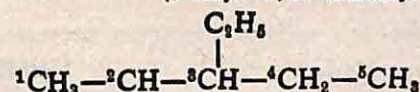
The application of these rules is demonstrated by naming the five isomers of hexane (C_6H_{14}).



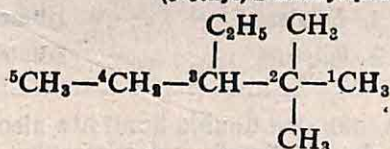
Now let us consider the name of some complicated compounds.



(5-ethyl-3, 3-dimethyl octane)



(3-ethyl, 2-methyl pentane)



(3-ethyl, 2, 2 dimethyl pentane)

1.8. ALKYL RADICALS

They can be regarded as alkane molecules with one hydrogen less. The name of an alkyl radical is fixed by using a number

indicating prefix for the number of carbon atoms in it as for an alkane and a group indicating suffix, —yl for alkyl radicals. Some examples of names of alkyl radicals is given below :

Parent simple alkane	Number of carbon atoms	Radical formula ($C_n H_{2n+1}$)	Radical name
Methane (CH_4)	1	CH_3-	Methyl—
Ethane (C_2H_6)	2	C_2H_5-	Ethyl—
Propane (C_3H_8)	3	C_3H_7-	Propyl—
Butane (C_4H_{10})	4	C_4H_9-	Butyl—
Pentane (C_5H_{12})	5	$C_5H_{11}-$	Pentyl— (also Amyl)
Hexane (C_6H_{14})	6	$C_6H_{13}-$	Hexyl—

The general formula for alkyl radicals is $C_n H_{2n+1}$ and they are often given the symbol $\cdot R$.

1.9. ALKENES AND ALKYNES

A hydrocarbon in which two of its consecutive carbon atoms are linked by a double or triple bond is known as unsaturated hydrocarbons. Simple unsaturated hydrocarbons are studied under the following two homologous series.

(1) Alkenes or Ethylenic hydrocarbons. Alkenes (also known as olefins) form a homologous series with general formula $C_n H_{2n}$. They contain a double bond which is formed by sp^2 hybridization. Formulae, common names and IUPAC names of the first few alkenes are given below.

Formula of olefin	Common name	IUPAC name
CH_2 (Unstable)	Methylene	Methene
$CH_2=CH_2$	Ethylene	Ethene
$CH_3-CH=CH_2$	Propylene	Propene
$CH_3-CH_2-CH=CH_2$	1-Butylene	1-Butene
$CH_3-CH=CH-CH_3$	2-Butylene	2-Butene

Compounds with more than one double bond are also known (e.g., alkadienes having two double bonds and molecular formula $C_n H_{2n-2}$, alkatrienes with three double bonds having molecular formula $C_n H_{2n-4}$).

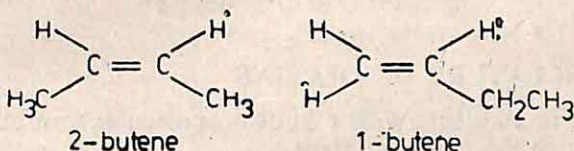
2. Alkynes or Acetylene hydrocarbons. Alkynes (also known as acetylenes) form a homologous series with general formula

C_nH_{2n-2} . They contain a tripple bond, which is formed by *sp* hybridization. Formulae, common names and IUPAC names of the first few alkynes are given below.

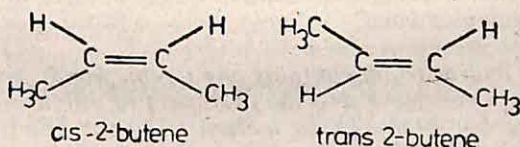
Formula	Common name	IUPAC name
$CH \equiv CH$	Acetylene	Ethyne
$CH_3C \equiv CH$	Methyl acetylene	Propyne
$CH_3C \equiv CCH_3$	Dimethyl acetylene	2-Butyne

1.10. ISOMERISM IN ALKENES

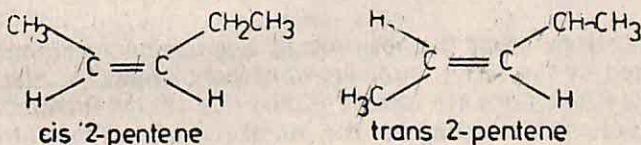
In the case of alkenes containing more than three carbon atoms, isomerism results from different positions of double bonds in the carbon chain. For example, butene can exist in two isomers.



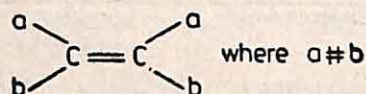
Such isomers in which the position of double bond is different are called position isomers. Since the double bond does not allow free rotation 2-butene can exist in two isomeric forms, *cis* and *trans*. This type of isomerism exhibited by *cis* and *trans* 2-butene is called geometrical isomerism.



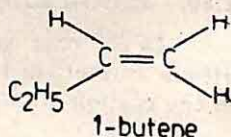
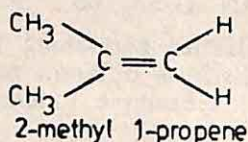
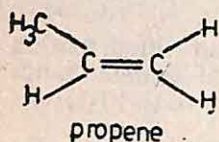
Likewise pentene, C_5H_{10} will also have the following two geometrical isomeric forms.



Geometrical isomerism can be exhibited only if two substituents on each carbon atom forming the double bond are different as shown below :



Thus, propene, 2-methyl-1-propene, 1-butene would not show cis-and trans-isomers.



1.11. NOMENCLATURE OF OLEFINS

The name of an olefin, with a known molecular formula, may be arrived through the following steps.

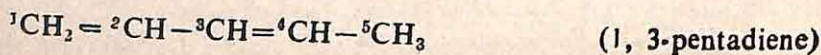
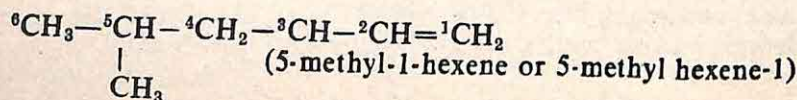
(1) *Select the longest chain of carbon atoms containing the double bond.* A larger chain without the double bond is not to be chosen.

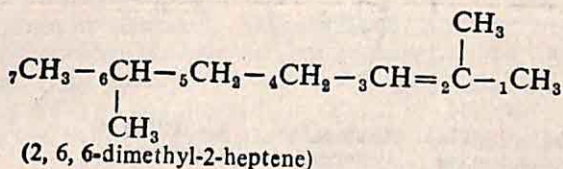
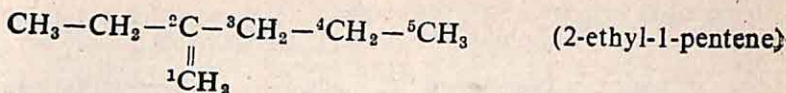
(2) *The carbon atoms of the selected chain are numbered from the end of the chain which gives smaller serial numbers to the carbon atoms linked by double bond.*

(3) *If the hydrocarbon contains one double bond per molecule, its name ends in -ene and the first part of the name indicates the number of carbon atoms in the molecule.* Thus, the first number of the series with two carbon atoms is called ethene or ethylene.

(4) *The place of a double bond is indicated by giving the serial number of the carbon atom in the chain where the double bond starts.*

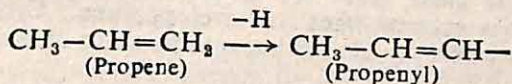
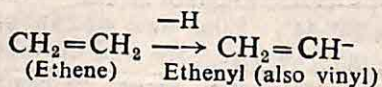
(5) *As in paraffins the positions of side chains in the molecule are indicated by the serial numbers of carbon atoms in the chain where these side chains are located. The side chains themselves are named as radicals according to the numbers of carbon atoms in them. The application of these rules is demonstrated by naming following compounds.*





1.12. OLEFINIC RADICALS

An olefinic molecule with one hydrogen atom less is called an **olefinic radical**. If the olefin has a double bond on the first carbon atom and the hydrogen atom is also removed from the first carbon atom, the radical takes a name from the olefin; For example :



Similarly, butene ($\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$) gives butenyl radical ($\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}\cdot$) and so on.

1.13. CYCLOALKANES

If the carbon chain of a saturated hydrocarbon molecule is joined to form ring, the hydrocarbons thus formed are called **cycloalkanes** or **cycloparaffins**. Their general molecular formula is C_nH_{2n} . Names and formulae of first four members are given below:

Cyclopropane C_3H_6 ; Cyclopentane C_5H_{10}

Cyclobutane C_4H_8 ; Cyclohexane C_6H_{12}

If we study the structure of cyclopropane (C_3H_6) we would observe that the carbon atoms occupy the corners of an equilateral triangle. Hence, the angle between any two valency bonds (involved in the formation of C—C linkages) is 60° (Fig. 1.6). However, we know that the four valencies of carbon atom are directed towards the four corner of a regular tetrahedron and angle between them is $109^\circ 28'$. Consequently, in cyclopropane there is a deviation of $109^\circ 28' - 60^\circ = 49^\circ 28'$ from valency angle. This means that each valency bond has been displaced through an angle of :

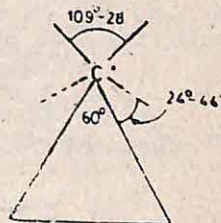


Fig. 1.6. Carbon atoms in cyclopropane.

$$\frac{1}{2} (109^\circ 28' - 60^\circ) = \frac{49^\circ 28'}{2} = 24^\circ 44'$$

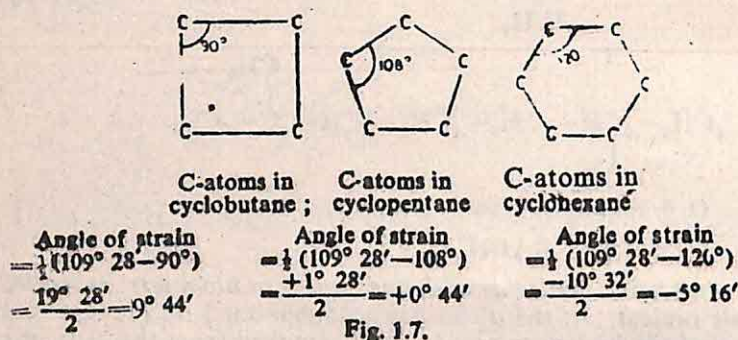


Fig. 1.7.

The angle through which each valency bond is displaced (from its normal position) is called angle of strain. Thus angle of strain for cyclopropane is $24^\circ 44'$. Like, wise we can calculate the angle of strain in cyclobutane, cyclopentane and cyclohexane (Fig. 1.7).

This, it is clear from the above values that strain goes on decreasing from cyclopropane to cyclopentane. Cyclopentane is found to be as stable as alkanes because its angle of strain is negligible.

It may be pointed out here that ring of higher members of cycloalkanes like cyclohexane can fold or plucker thereby allowing the retention of the normal tetrahedral angle between C—C bonds. Thus a cyclohexane ring can fold in two different ways giving the boat and chair conformations as shown in Fig. 1.8.

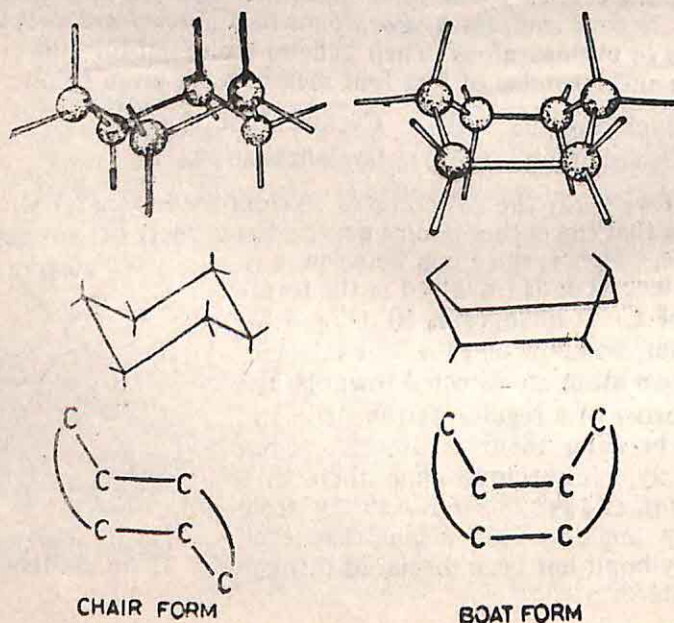


Fig. 1.8. Chair and boat conformation of cyclohexane.

The chair form is more stable and the energy difference between the two conformations is about 44 kJ mol^{-1} .

1.14. ARENES

Arenes or aromatic hydrocarbons are compounds containing the basic carbon skeleton of hydrocarbon called benzene (C_6H_6). They have the general formula $\text{C}_n\text{H}_{2n-y}$ where y is the number of benzene rings in the molecule. Thus, in benzene $n=6$, $y=1$ and the formula is C_6H_6 , in naphthalene $n=10$, $y=2$ and the formula is C_{10}H_8 .

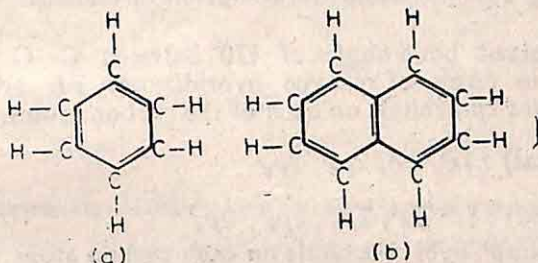


Fig 1.9. (a) Benzene molecule, (b) naphthalene molecule.

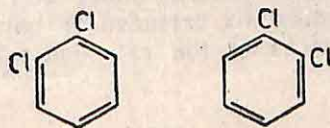
1.15. STRUCTURE OF BENZENE

Taking all the evidence into consideration, Kekule (1865) was the first to suggest the *ring structure for benzene with alternate single and double bonds* (Fig. 1.9 (a)). This structure, however, possesses following shortcomings :

(i) Benzene having three double bonds should behave like a highly unsaturated compound, but actually it is found to behave like a saturated hydrocarbon, forming substitution compounds readily.

(ii) Kekule formula contains two kinds, of bonds, single and double between carbon atoms. Therefore, it is expected to have different bond lengths between its carbon atoms, *i.e.* ($\text{C}-\text{C}$, 1.54 \AA and $\text{C}=\text{C}$, 1.34 \AA). Actually from X-ray studies it has been found that all the bonds of benzene are of equal lengths (1.39 \AA) and the bond angle between $\text{C}-\text{C}$ is 120° .

(iii) Kekule formula admits the formation of two disubstitution products for similar substituents *e.g.*, the two orthodichlorobenzenes possible would be :



However, actually only one orthodichlorobenzene is known.

To overcome these objections Kekule suggested that the double bonds of benzene ring oscillate between two possible structures and benzene is actually a resonance hybrid of the two forms shown below.

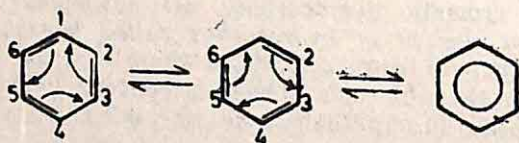


Fig. 1'10. Resonance hybrid structure of benzene.

The observed bond angles of 120° between C—C atoms can be explained in terms of sp^2 type hybridization of carbon atoms leaving one pure $2p$ -orbitals on each of the carbon atoms.

C (normal) : $1s^2, 2s^2, 2p_x^1, 2p_y^1$

C (excited) : $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

The three sp^2 hybrid orbitals on each carbon atom are used to form two sigma bonds with the adjacent carbon atoms and one with an hydrogen atom (see Fig. 1'11). The six unhybridised (or pure)

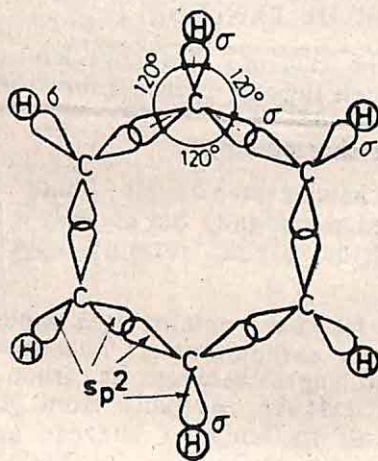


Fig. 1'11. The formation of σ skelton of benzene.

$2p$ -orbitals, each having one electron, are perpendicular to the plane of the carbon skelton and they are quite close enough to allow a side-way overlap of their electron clouds, above and below the plane of σ bonded skelton yielding six extended π bonds (Fig. 1'12). It should be emphasized here that the extended π bonds are delocali-

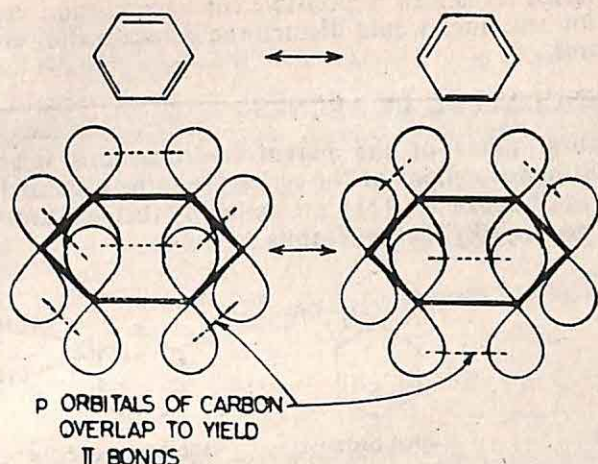


Fig. 1·12. $2p$ -orbitals overlap to form extended bonds (non-localized).
zed (or spread over) on all the six carbon atoms giving a cloud of negative charge above and below the plane of the carbon skeleton (see Fig. 1·13.)

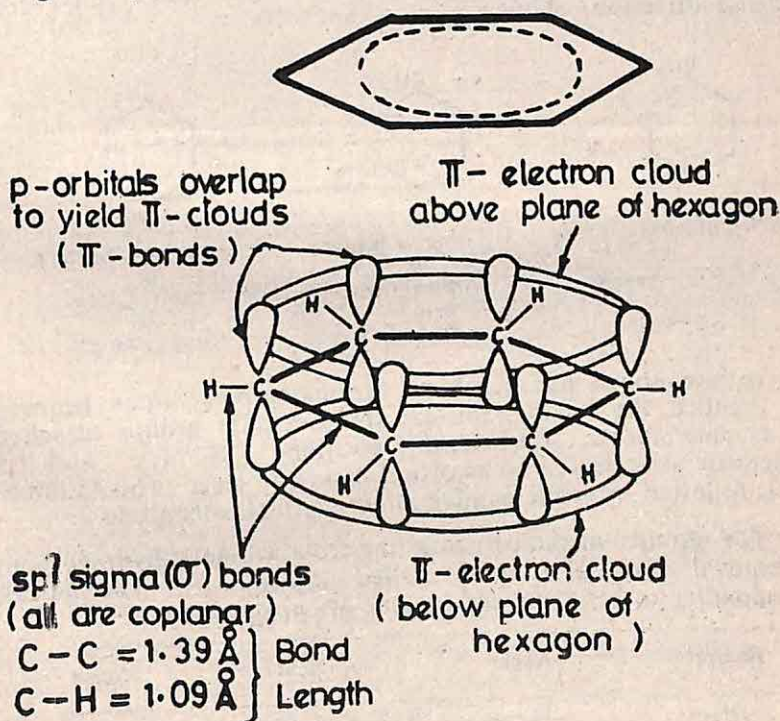


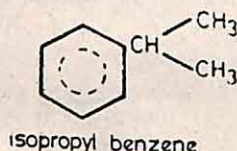
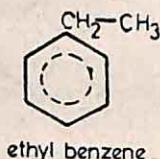
Fig. 1·13. The delocalized π -orbital in benzene.

Extensive delocalized confers extreme stability to the benzene molecule and is directly responsible for its resistance to undergo

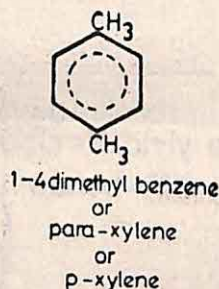
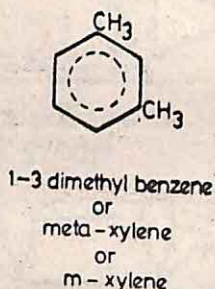
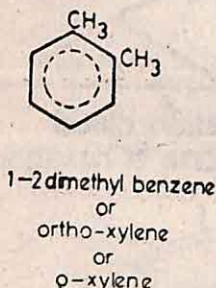
chemical reactions, It is also responsible for substitution reactions because addition reactions would disturb the delocalization over the six carbon atoms.

1.16. NOMENCLATURE IN ARENES

The natural name of the parent hydrocarbons is benzene, (C_6H_6). Other hydrocarbons of the series are to be regarded as the alkyl derivatives of benzene. They are called by their natural names or may be named as alkyl benzene thus :



In higher homologues of benzene having two or more alkyl groups on the benzene ring, the position of the alkyl groups are indicated by numbering the corners of the ring as 1, 2, 3, 4, etc. in clockwise direction. Thus :



In the above hydrocarbons the six-carbon atom benzene ring is called the benzene nucleus and the alkyl groups attached to it as side chains. Further, the positions 1, 2 ; 1, 3 and 1,4 respectively are referred to as ortho, meta and para. This terminology is followed up while naming all derivatives of benzene.

The groups of radicals resulting from aromatic hydrocarbons by removal of one H atom are called aryl radicals. The radicals corresponding to benzene and toluene are given below :—

Radical	Name	Radical	Name
C_6H_5-	Phenyl	$C_6H_5.CH_2-$	Benzyl
$C_6H_4CH_3-$	Tolyl	$C_6H_5.CH<$	Benzal

QUESTIONS

(A) Essay-type

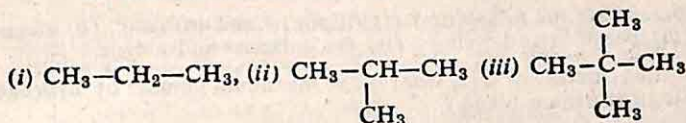
1. What do you know about the vital force theory of organic substance?

2. What are the current main theories of organic chemistry? Why did it become necessary to study organic substances separately from other substances?

3. Explain the following terms: (i) Isomerism, (ii) polymerisation (iii) cracking and (vi) homologous series.

4. What is meant by isomerism? Describe the various types of isomerism.

5. Give the common and systematic names of the following substances:

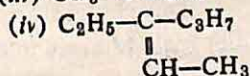
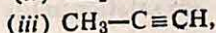
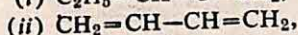
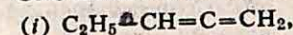


6. Write the structural formulae for the following substances. (i) 4-ethyl heptane, (ii) 4-ethyl 2, 2-dimethyl heptane, (iii) 3-ethyl, 4-propyl octane.

7. Write the structural formulae and systematic names for the isomers of hexane.

8. Give the structural formulae of the following. (i) Isobutene; (ii) 2-methyl-2-butene; (iii) ethyl acetylene; (iv) 2-butyne.

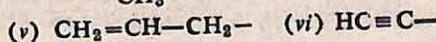
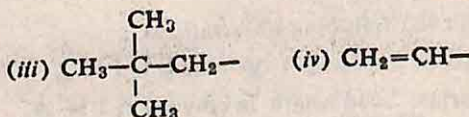
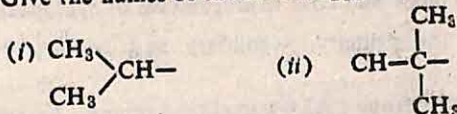
9. Give the names for the following structures:



10. Give the structural formulae and names of the isomers having under mentioned molecular formulae. (i) C_5H_{10} , (ii) C_5H_8

11. Give the structural formulae of the following cycloalkanes. (i) cyclopropane, (ii) cyclobutane, (iii) cyclopentane and (iv) cyclohexane.

12. Give the names of the following groups.



13. Write a detailed note on the strain theory applied to cycloalkanes.

14. Discuss the structure of benzene.

15. Draw structure of (i) dinitrobenzene, (ii) m-nitrotoluene, (iii) 4-chloro-2, 3-dinitrotoluene, (iv) 2, 4, 6, trinitrophenol.

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16. Draw the structures for all the isomeric homologues of benzene with the formula C_8H_{10} . Assign acceptable name to each.

(B) Short Answer Type :

17. What unique properties of carbon make possible the formation of a large number of organic compounds ?

18. General formula of alkanes is C_nH_{2n+2} . What is the general formula for alkynes and arenes ?

19. Classify each of the following as a homologue of methane, ethylene or benzene series : $C_{10}H_{18}$, C_7H_{14} , $C_{22}H_{46}$, C_9H_{16} and C_7H_8

20. Can homologues be isomers ? Explain.

21. What similarities are expected amongst homologues.

22. Differentiate the following ? (i) Aliphatic and aromatic, (ii) alkanes and alkenes, (iii) paraffins and olefins, (iv) cycloalkanes and arenes.

23. In the structure of CH_4 what is the maximum number of hydrogen atoms which lie in the same plane ?

24. Can isomeric butanes be distinguished by the number of monohalogen derivatives they give ? Explain.

25. Cis-trans isomerism is encountered in olefins and cycloalkanes. Explain.

26. How many structural isomers are possible for C_4H_8 ? Which will show geometrical isomerism ?

27. Which of the following will show geometrical isomerism. (i) Pentene-2, (ii) 1-chloropropene, (iii) 1-chloro-2-methyl-2-butene, (iv) pentene-1.

28. Is it proper to say that absolutely free rotation exists in carbon-carbon single bond ? Why ?

29. Define angle of strain. What is the angle of strain in cyclobutane ?

30. Alkenes and cycloalkanes have the same general formula. In what important ways they differ in their structure ?

31. Is it correct to say that benzene is saturated ?

32. Explain why was it difficult to assign a structure of benzene in agreement with its properties ?

33. Draw the chair and boat conformation of cyclohexane.

34. Pick up the primary, secondary and tertiary carbons in the following.

2 methyl-3 ethyl hexane ; 3,3,4-trimethyl heptane ; 3-isopropyl hexane.

35. Account for the following observations :

(i) Carbon-carbon bond length in ethane is 1.54 \AA .

(ii) Carbon-carbon bond length in ethylene is 1.34 \AA .

(iii) Carbon-carbon bond length in benzene is 1.39 \AA .

(C) Objective type :

36. Put tick mark for the correct answer.

(a) Which one of the following is not an organic compound ?

(i) Hexane, (ii) urea, (iii) ammonium cyanate, (iv) spirit.

(b) Ethylene contains : (i) 5 σ and one π bonds, (ii) 3 σ and 2 π bonds, (iii) 11 σ and one π bonds (iv) 9 σ and 2 π bond.

(c) Acetylene contains : (i) 11 σ and one π bonds (ii) 3 σ and 2 π bonds (iii) 9 σ and 2 π bonds (iv) 4 σ and 4 π bonds.

(d) Compounds having same number and kind of atoms but a different arrangement of atoms in the molecules are known as : (i) isotopes (ii) isobars (iii) isomorphs.

(e) Geometrical isomerism is possible in case of (i) pentane (ii) propane (iii) butene-2, (iv) ethane.

(f) Which of the following statements explains as to why carbon forms a large number of compounds? (i) carbon has a variable valency (ii) carbon has great chemical affinity, (iii) property of catenation, (iv) all the above.

(g) The structural formula of an organic compound represents : (i) its composition, (ii) its characteristics, (iii) the nature of the functional group (iv) the arrangements of atoms in the molecules.

(h) Which one of the following statements is false? All the members of the homologous series of alkanes (i) have general formula C_nH_{2n+2} , (ii) have almost similar physical Properties (iii) have almost similar chemical Properties, (iv) are prepared by almost similar methods.

Sources and Synthesis of Hydrocarbons

2.1. INDUSTRIAL SOURCES OF HYDROCARBONS

The two chief sources of hydrocarbons are *petroleum* and *coal tar*. Most of the aliphatic hydrocarbons are obtained from petroleum. Natural gas (a mixture of alkanes and alkenes) comes out along with the petroleum from the earth. Large volumes of hydrocarbons are obtained during the cracking of petroleum. Hydrocarbons constitute excellent raw materials for numerous compounds called *petrochemicals*. The hydrocarbons are changed into different compounds which are used as solvents, explosives, insecticides, pesticides, medicines, soaps, artificial fats, etc. In the Table 2.1 below are listed the hydrocarbons isolated from petroleum and the compounds obtained from them.

Coaltar is one of the chief sources of organic compounds and is obtained by the destructive distillation of coal, i.e., heating coal to high temperature in absence of air. At one time it was the only major source of aromatic hydrocarbons, but now many of these are obtained from petroleum as well.

Petroleum (Pefra=rock and oleum=oil) or mineral oil is a dark greenish-brown, viscous oil found deep in earth's crust. It is mainly composed of various hydrocarbons (like straight-chain paraffins, cycloparaffins or naphthenes, olefins and aromatics) together with small amounts of organic compounds containing oxygen, nitrogen and sulphur. The average composition of crude petroleum is : C=79.5 to 87.1% ; H=11.5 to 14.8% ; S=0.1 to 3.5% ; N and O=0.1 to 0.5%.

The oil is usually floating upon a layer of brine and has a layer of gas on top of it.

Table 12.1. *Compounds obtained from hydrocarbons of petroleum.*

<i>Hydrocarbons</i>	<i>Compound obtained</i>	<i>Uses of the compound</i>
1. Methane	Methanol Chloromethanes Acetylene Dimethyl sulphate	Solvent Solvent Illuminant Synthesis
2. Ethane	Acetic acid Diethyl ether Acetic anhydride Nitroethane	For acetylation Solvent For acetylation Explosive
3. Ethylene	Ethanol Butadiene Ethylene glycol Propanal	Solvent Rubber industry Polymer plastics Solvent
4. Propane	Propionic acid Nitromethane Acetone	Synthesis Explosive Solvent
5. Propene	Allylchloride Allyl alcohol Glycerol	Polymers Synthesis Explosive
6. Pentene	Butanol Butadiene Iso-octane	Solvent Rubber industry Gasoline industry
7. <i>n</i> -Hexane	Benzene D.D.T. Gammexane	Synthesis of aromatics Insecticide Pesticide
8. <i>n</i> -Heptane	Toluene	Synthesis
9. Arenes	Benzene Toluene Xylenes	For TNT and other synthetic uses

Classification of petroleum. The chemical nature of the crude petroleum varies with the part of the world in which it is found. There appears, however, to be three principal varieties :

(1) **Paraffinic base type crude** is mainly composed of the saturated hydrocarbons from CH_4 to $\text{C}_{35}\text{H}_{72}$ and little of the naphthenes and aromatics. The hydrocarbons from $\text{C}_{18}\text{H}_{38}$ to $\text{C}_{35}\text{H}_{72}$ are semi-solids called 'waxes'.

(2) **Asphaltic base type crude** contains mainly cycloparaffins or naphthenes with smaller amounts of paraffins and aromatic hydrocarbons.

(3) **Mixed base type crude** contains both paraffinic and asphaltic hydrocarbons and generally are rich in semi-solid waxes.

Origin of petroleum. According to modern theory petroleum has resulted from the partial decomposition of marine animals and vegetable organisms of pre-historic forests. Changes in earth's crust (like volcanoes, etc.) had buried these material underground, where they have been subjected to intense pressure and heat during the ages of time. The conversion of these materials into various hydrocarbons has been going on either under the influences of radioactive substances like uranium or by the bacterial decomposition under high pressure.

Petroleum resources The world resources of crude oil are estimated at 30,000 million tonnes, of which Indian reserves are only 100 million tonnes. The biggest oil producing country of the world is USA, which produces about 70% of the total world output. Other countries in the order of the total production are USSR, Venezuela, New Guinea, Mexico, Rumania, Iraq, Burma, Pakistan and India. The chief oil production centres in India are Rudrasagar and Lakwa (in Assam) and Ankleshwar and Kalol (in Gujarat). Oil and Natural Gas Commission of India in collaboration with some other foreign companies has undertaken to explore petroleum in Persian Gulf and Gulf of Kutch along India's coast in sea water. Indication of economical availability of petroleum in Bombay area are rated high. Our petroleum refineries are located at Gauhati (Assam), Barauni (Bihar), Koyali (Gujarat), Cochin, Madras, Haldia, Trombay (Near Bombay), Vishakhapatnam. A new refinery is being set up at Mathura (U.P.)

Mining of petroleum. The oil usually floats upon a layer of salt water and has a layer of natural gas upon it. It is present deep below impervious rocks. Mining of oil is done by drilling holes in the earth's crust and sinking pipes up to the oil-bearing

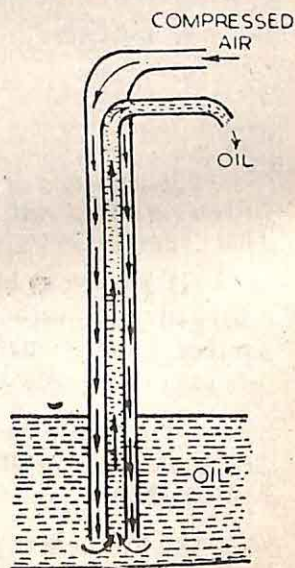
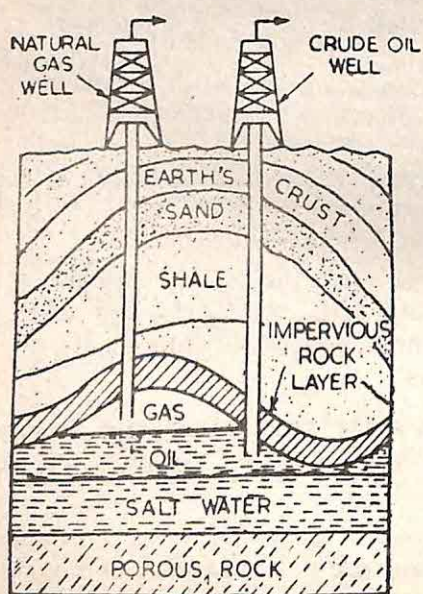


Fig. 2.1. (a) Mining of oil. (b) Air lift pump.

porous rocks. Oil usually gushes out itself due to hydrostatic pressure of natural gas. Alternatively, it may be mechanically pumped up by using either lift-pumps or air forcing lift pump. The latter consists of two co-axial pipes lowered into the base of oil bed. Compressed air is forced through the outer pipe whereby oil comes out through the inner pipe (see Fig. 2.1 (a) and (b)).

Refining of crude petroleum involves the following steps :

Step 1. Separation of water (Cottrell process). The crude oil from the oil well is an extremely stable emulsion of oil and salt water. The process to free the oil from water consists in allowing the crude to flow between the two highly charged electrodes. The colloidal water droplets coalesce to form drops that separate out from the oil.

Step 2. Removal of harmful sulphur compounds involves in treating oil with copper oxide. A reaction occurs with sulphur compounds, which results in the formation of copper sulphide, a solid, which is then removed by filtration.

Step 3. Fractionation. The crude oil is then heated to about 675K in an iron still (which is heated either electrically or in a fire box) whereby all constituents except the residue (asphalt or coke) are evaporated. The hot vapours are then passed through a "fractionating column", which is tall cylindrical tower containing a number of horizontal stainless steel trays. Each tray is provided with small chimney which is covered with a loose cap. As the vapours go up they become gradually cooler and fractional condensation takes place at different heights of column. High boiling fractions condenses first ; while the low boiling fraction turn by turn. Various principal fractionation products thus obtained are given in Table 12.2.

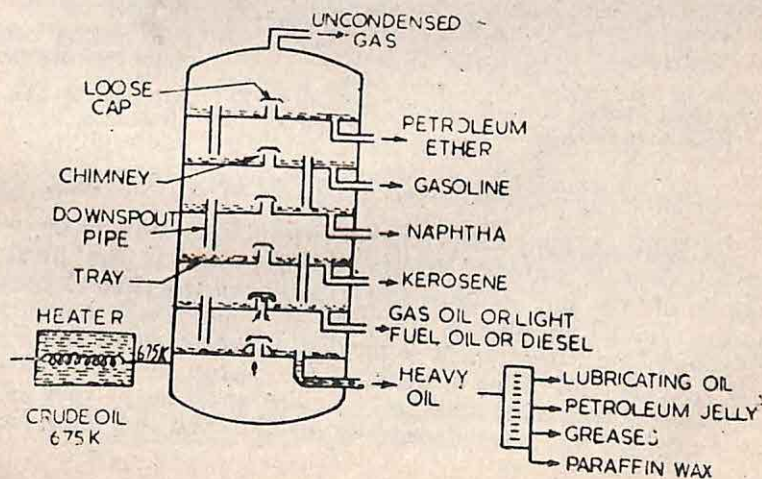


Fig. 2.2. Fractionation of crude oil.

Table 12.2.

Typical fractionation of petroleum.

Fraction	Boiling point range	Composition	Approximate %	Uses
1. Uncondensed gases	273 to 303K	C ₁ to C ₄	2	As fuel, for making carbon for rubber industry, manufacture of gasoline (by polymerisation), hydrogen.
2. Crude naptha :	303 to 423K	C ₅ to C ₁₁		
(i) Petroleum ether	303 to 343K	C ₅ to C ₇	2	As a solvent in varnish and rubber industries, for dry cleaning.
(ii) Gasoline	343 to 393K	C ₇ to C ₁₁	~	Motor fuel, dry cleaning, for making petrol air gas.
(iii) Solvent naptha or benzine	393 to 423K	—		In dry cleaning solvent, also as a solvent for varnishes, paints, fats and oils.
3. Kerosene oil	434 to 573K	C ₁₁ to C ₁₆	18	For illumination, for making oil gas and as domestic fuel, as disinfectant.
4. Gas oil, fuel oil or diesel oil	573 to 603K	C ₁₁ to C ₁₆	20	Fuel for diesel engines, for conversion to gasoline by cracking.
5. Heavy oil :	603 and above			
(i) Lubricating oils	—	C ₁₇ to C ₃₀	30	For lubricating machines.
(ii) Vaseline (Petroleum jelly)	—			For making toilet creams, ointments and medicines.
(iii) Greases	—	—	—	As lubricant.
(iv) Paraffin wax	—	—	—	For making candles, water proofing fabrics.
6. Petroleum coke (Residue in still)	—	Essentially graphite	10	Artificial asphalt, fuel electrodes.

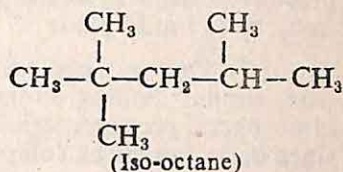
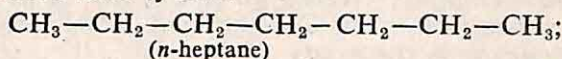
2.3. FUEL KNOCK—OCTANE AND CETANE NUMBER

An internal combustion engine (within an automobile) works with a system of pistons. In the down stroke of the piston, a mixture of air and gasoline vapour is drawn from the carburettor into the cylinder and in the upstroke the mixture is compressed. *The ratio of the initial volume to the final volume is called compression ratio.* At the end of the upstroke of the piston, a spark ignites the compressed air-gasoline mixture. As the gases burn, they expand and the flame front moves in smooth manner and supplies power to the engine.

For maximum efficiency of the engine, a high compression ratio is required. But as the compression ratio increases, the gasoline-air

mixture burns in an explosive manner and thus produces a metallic sound called knocking and this indicates inefficient performance of the gasoline.

Various hydrocarbons have different knocking tendencies. The calibration or rating of various fuels in accordance to these knocking properties is done in terms of a unit called the octane number. *Iso-octane* or 2-2-4-trimethylpentane was found to possess excellent anti-knock property. This was arbitrarily assigned a value of 100; whereas *n-heptane* which is very prone to knocking was assigned a value of zero.



All fuels were graded in between these two values by comparing with a suitable mixture of the above two compounds. **Octane number of a gasoline (or fuel) is defined as the percentage of iso-octane mixed with *n*-heptane that has the same knocking characteristics as the fuel under examination.** Thus, a fuel having an octane number of 80 behaves in a manner similar to a mixture having 80% of iso-octane and 20% *n*-heptane.

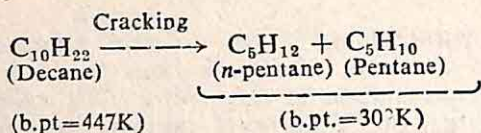
In high compression engines, fuels having an octane number 80 is required. Knocking is minimised by adding tetra ethyl lead, $\text{Pb}(\text{C}_2\text{H}_5)_4$ or TEL which is known as "an antiknock compound". Diesel fuel is very different from ordinary fuel for it usually consists of kerosene and heavy lubricating oils. The construction of a diesel engine is different and in this case high octane fuels are less efficient than lower ones. The efficiency of a diesel fuel is expressed in terms of a unit called the cetane number. Cetane or *n* hexadecane is assigned a value of 100 and α methyl naphthalene that of zero. **Thus, cetane number of a given fuel is the percentage of cetane in a mixture of cetane and α -methyl naphthalene which matches in ignition quality with the given sample of fuel.**

2.4. PROCESSES IN PETROLEUM INDUSTRY

Gasoline is the most important fraction of crude petroleum since this is used as a motor fuel. Crude petroleum contains a very small percentage of it. Hence, various methods have been devised to raise the yield of this fraction and to convert other fractions into this low boiling fuel. Some of the important ones are as follows :

(1) **Cracking.** Thermal decomposition of paraffins or pyrolysis of hydrocarbons to give low molecular mass hydrocarbons with lower boiling points is termed *cracking*. By this process the bigger higher boiling molecules are converted into desired ones. This is

usually carried out at high pressure and temperature in presence of a catalyst like silica-alumina or silica-alumina-thoria :

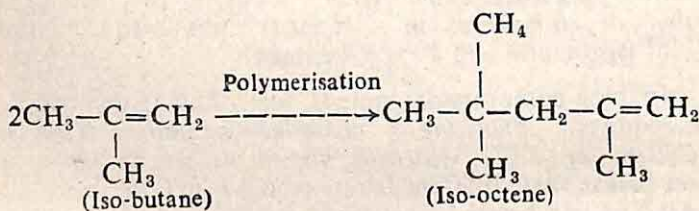


The cracking is of two main types :

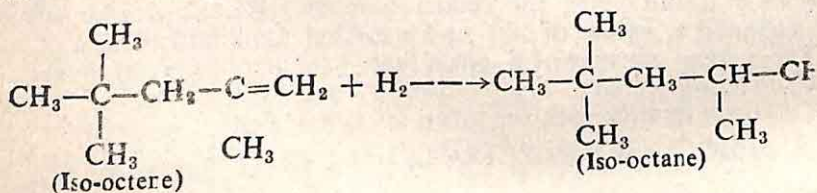
(i) *Liquid phase cracking.* Heavy oil is cracked by heating at a suitable temperature (750 to 800K) under 7 to 68 atmospheric pressure. High pressure is necessary to maintain the cracked material in liquid phase.

(ii) *Vapour phase cracking.* Kerosene oil or any other oil with similar boiling range is heated to 870K under 3.5 to 10 atmospheric pressure. Heavy oils cannot be cracked by this method since these cannot be completely vaporised under these conditions.

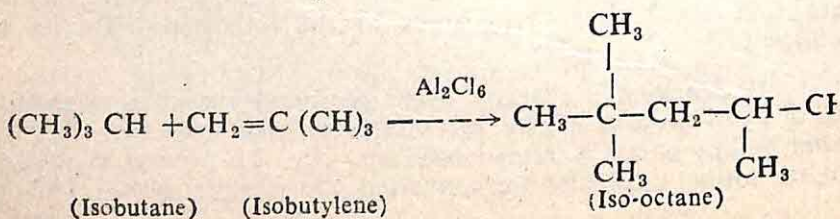
(2) *Polymerisation.* Many smaller alkanes occur in petroleum and many more are produced during cracking. These are polymerised (usually dimerised) by heating in presence of phosphoric acid.



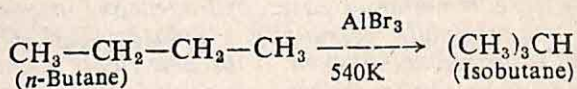
By hydrogenation, the dimers can be converted to iso-octane. This also raises the octane number of the gasoline.



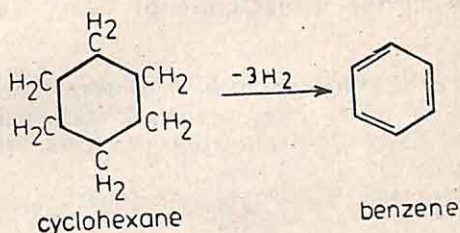
(3) *Alkylation.* At high temperatures in presence of catalyst like H_2SO_4 or anhydrous Al_2Cl_6 , an alkane can add to a double bond of alkene to give a bigger molecule of higher octane value.



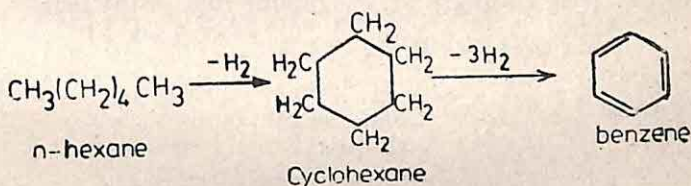
(4) **Isomerisation.** *n*-Butane occurs in large concentrations both in natural and thermally cracked gas. This in presence of a catalyst AlBr_3 could be converted to the extent of 75 to 80 percent into isobutane. Isobutane is very valuable starting material for making high octane hydrocarbons by polymerisation, alkylation, etc.



(5) **Reforming.** Sometimes the octane number of a straight-run gasoline is raised by catalytic cracking. For this gasoline is heated to about 880 K under 28–50 atmospheric pressure in presence of a catalyst which causes (i) dehydrogenation of cyclohexane and related compounds

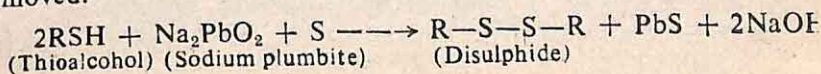


and (ii) cyclisation of alkanes to cycloalkanes and then subsequent dehydrogenation.



Rise in octane number is partly due to increased content of benzene and toluene. The process is called *reforming* or *catalytic cracking*.

(6) **Refining of gasoline.** The gasoline obtained by the fractionation of crude petroleum is known as straight-run gasoline. This gasoline may have octane values ranging from 20 to 73. The octane value of the gasoline can be improved by adding antiknock compound but the presence of colour, odour and sulphur compounds lowers its response to antiknock compounds. To remove sulphur compounds (e.g., thioalcohols—RSH) gasoline is washed with concentrated sulphuric acid or sodium hydroxide. If necessary, washed gasoline is further treated with alkaline sodium plumbite, which oxidises thioalcohol to disulphides which may be removed.

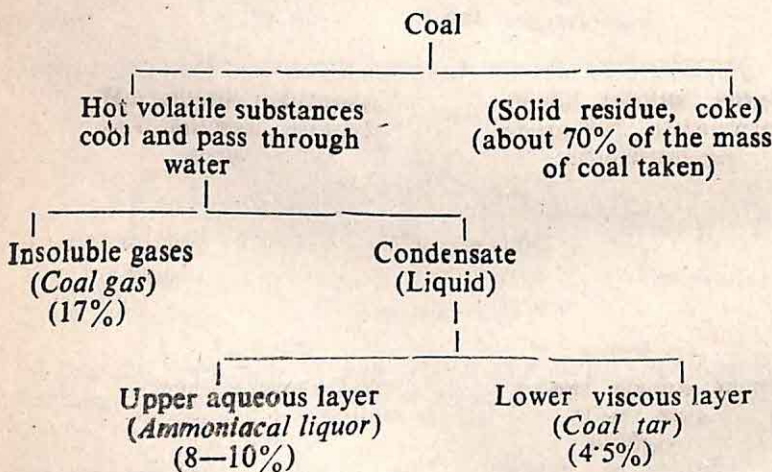


2.6. PYROLYSIS OF COAL

Coal is believed to be formed by the remains of vegetable matter which got buried under the earth in the prehistoric times. Under the influence of great pressure and heat it lost moisture and decomposed by the elimination of gases, hydrogen and oxygen. The plant material was originally essentially cellulose; $(C_6H_{10}O_5)_n$, but with the loss of hydrogen and oxygen it became richer in carbon and thus converted to coal. In India large quantities of coal are being mined at Jharia, Raniganj, Bokaro, Giridih, Karanpura and in Assam.

Coal is not merely free carbon, but also contains a complex mixture of some 200 odd organic compounds. These compounds are isolated by the process of pyrolysis and are used as solvents, preservatives and in the manufacture of dyes, drugs, perfumes, explosives, etc.

The process of heating coal at high temperatures (1270 to 1470 K) in the absence of air is called **pyrolysis, destructive distillation or carbonization of coal**. The following products are obtained by the pyrolysis of coal.



The fraction obtained by the pyrolysis of coal are used for different purposes *e.g.*, coke in the blast furnaces in iron industry and coal gas as fuel. Coal tar, a black viscous liquid with unpleasant smell, is further refined by distillation. Distillation products are separated into different fractions with different boiling ranges. The same has been tabulated in Table 2.3.

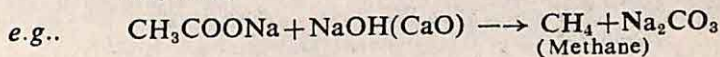
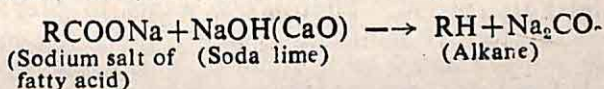
Table 2.3. *Fractions of coal tar.*

Name of fraction	B. pt. range	sp gravity (g cm ⁻³)	Percentage by volume	Chief compounds
1. Light oil	upto 443K	0.95	2.25	Benzene, toluene, xylene, pyridine
2. Middle oil (carbonic oil)	443-503K	1.00	7.5	Phenol, naphthalene
3. Heavy oil (creosote oil)	503-543K	1.03	16.5	Cresols
4. Green oil (anthracene oil)	543-633K	1.08	12	Anthracene, naphthalene phenanthrene
5. Pitch (black residue)	Left in distillation retort	—	56	Carbon

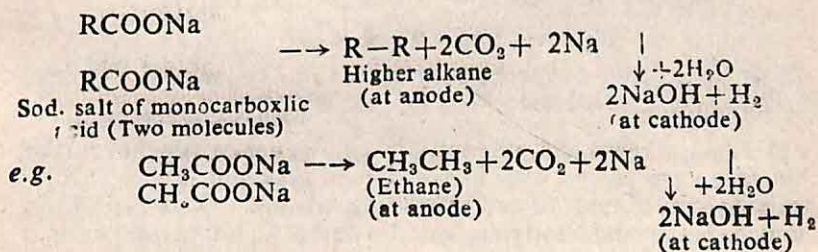
2.7. LABORATORY PREPARATION OF ALKANES

Alkanes can be prepared in the laboratory by the following methods.

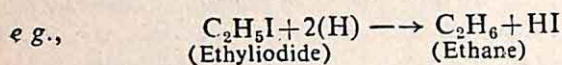
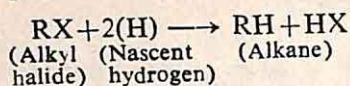
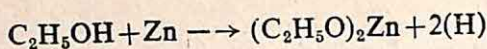
(1) **Form acids.** (a) *By decarboxylation.* The sodium salts of alkyl carboxylic acid (where R=alkyl group) on heating with soda lime (NaOH+CaO) are *decarboxylated* to give alkanes.



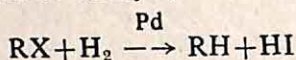
(b) *By Kolbe's electrolytic method.* When an aqueous solution of sodium or potassium salt of mono-carboxylic acid is electrolysed, a higher alkane is obtained at the anode.



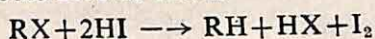
(2) **From alkyl halides.** (a) *By reduction.* (i) Alkyl halides are reduced by nascent hydrogen (produced by the action of ethyl-alcohol on Zn—Cu couple) to alkanes.



(ii) The alkyl halide can also be reduced by hydrogen in presence of palladium as catalyst,

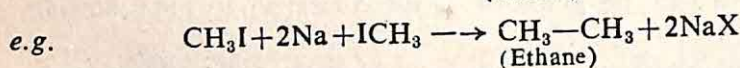
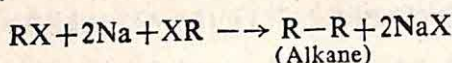


(iii) The reduction can also be carried out by heating alkyl halide with hydroiodic acid at 420K.

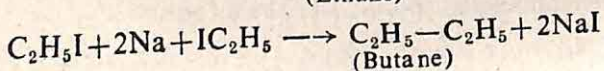
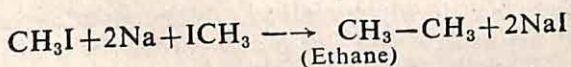
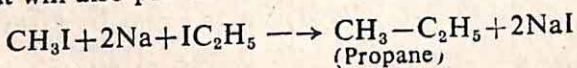


Iodine produced in this reaction can react with alkanes. It is, therefore, removed by addition of red phosphorus.

(b) By *Wurtz reaction*. The alkyl halides (preferably bromides and iodides) react with metallic sodium in presence of dry ether to produce alkanes.

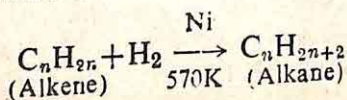


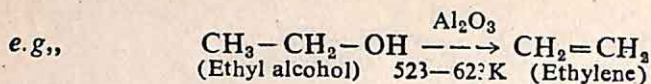
This method is suitable for the preparation of symmetrical alkanes. A mixture of products is obtained when two different alkyl halides are reacted. Thus, if one wants to prepare propane, a mixture of methyl iodide and ethyl iodide in equimolecular proportions are reacted with sodium. This will not produce only propane but will also produce ethane and butane along with it.



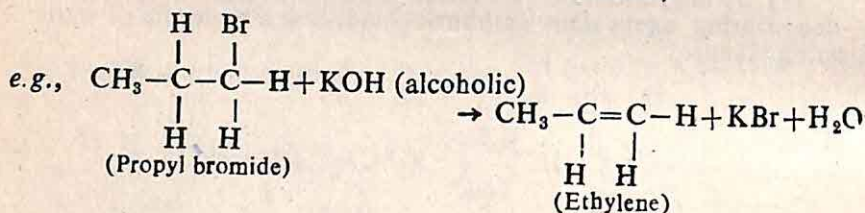
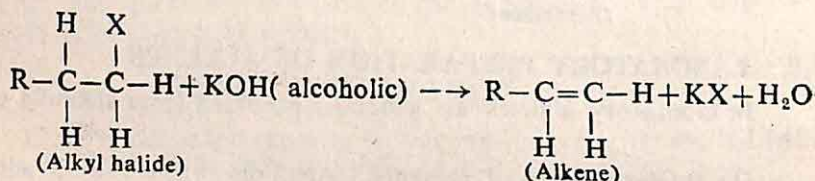
Now to get pure propane, mixture is to be separated. Hence, this method is of limited use in the laboratory.

(3) **From alkenes and alkynes.** When alkenes or alkynes mixed with hydrogen are passed over finely divided nickel at about 570K, they are hydrogenated to corresponding alkanes. This method is known as Sabatier and Senderen reaction and is an important method for preparation of alkanes.





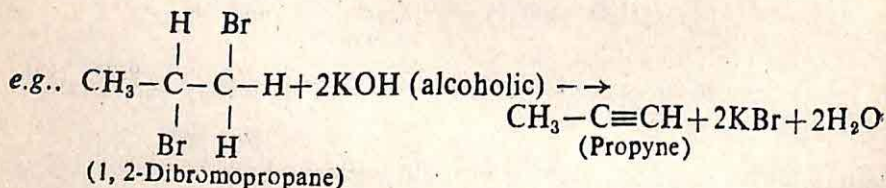
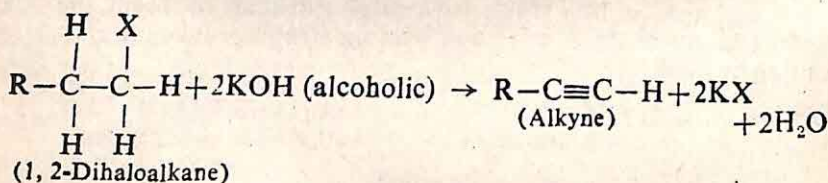
(2) **By dehydrogenation of alkyl halides.** When heated with alcoholic solution of potassium hydroxide, alkyl halides eliminate a hydrogen and halogen atom from adjacent carbon atoms to form alkenes.



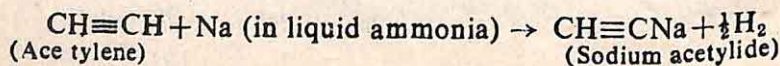
This is the most important method of preparing alkenes in the laboratory.

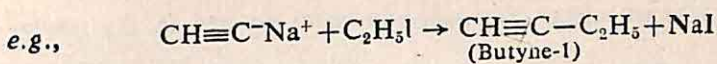
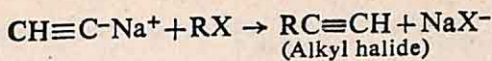
2.9. LABORATORY PREPARATION OF ALKYNES

(i) **From vic dihalides.** Dihalides having two halogen atoms attached to consecutive carbon atoms are known as vicinal or vic-dihalides. Vic dihalides on boiling with alcoholic potash are converted to alkynes.

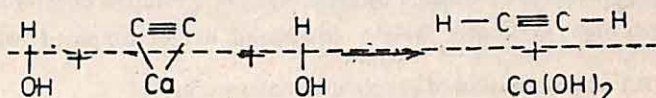
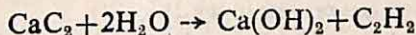


(ii) Alkynes are generally prepared from acetylene, the first member of this series. For this acetylene is first treated with sodium metal in presence of liquid ammonia when sodium acetylide is produced, which on treatment with alkyl halide yield higher alkynes.





In laboratory acetylene is generally prepared by the action of water on calcium carbide.



QUESTIONS

(A) Essay Type

1. Describe the views held about the origin of natural petroleum.
2. How does petroleum occur in nature? Describe briefly the process of petroleum refining.
3. What end products are obtained as a result of fractional distillation of petroleum and to what use are they put?
4. Explain the terms : (i) Cracking. (ii) Octane number. (iii) Reforming.
5. Write a descriptive note on synthetic petrol.
6. What do you understand by pyrolysis of coal? What are the fractions obtained from it?
7. Describe the destructive distillation of coal-tar and name the important commercial products obtained from coal-tar.
8. Write short notes on the following : (i) Anti-knock compounds. (ii) Knocking. (iii) Cetane number.
9. Describe general methods of preparing alkanes in the laboratory.
10. Describe general methods of preparing alkenes in the laboratory.
11. Write general methods of preparing alkynes in the laboratory.
12. What do you understand by the term petrochemicals. What are the hydrocarbons obtained from it and changed into different useful compounds?

(B) Short-Answer Type

13. What is the composition of natural gas? What is its main use?
14. What is the difference between petrol and petroleum? Name the lead compound added to gasoline to improve the quality. Is it desirable to add lead compounds to gasoline?
15. What is IUPAC name of 'iso-octane'?
16. State which compound in each pair would be expected to have higher octane number? (i) *n*-heptane or *n*-butane, (ii) 2, 4-dimethyl hexane or 2-methyl heptane, (iii) 2, 2, 4-trimethyl pentane or octane, (iv) cyclohexane or benzene.
17. A sample of gasoline has an octane Number 93. Explain clearly what does this mean?

18. How can a "high octane" gasoline be obtained other than by adding lead tetraethyl or similar compounds?

19. Why are sulphur containing compounds removed in the refining of gasoline?

(C) *Objective Type:*

20. Put a tick mark for the correct answer:

(a) Pyrolysis is a process in which

(i) alkanes are produced by electrolysis of a solution of fatty acid.

(ii) high molecular weight compound is decomposed when heated strongly.

(iii) polymerisation of simple molecules occur.

(iv) pyrosulphuric acid is formed.

(b) Crude oil rich in naphthenes is called (i) asphaltic. (ii) paraffinic. (iii) alkenes, (iv) none of the above.

(c) Which one of the variety of coal contains maximum percentage of carbon? (i) Lignite. (ii) Bituminous. (iii) Anthracite.

(d) Which one of the following constituents does not belong to crude naphtha? (i) Petroleum ether, (ii) Gasoline. (iii) Ligroin. (iv) Gas Oil.

(e) The reaction,



(Where R=alkyl group and X=halide) is an example of (i) Kolbe's reaction, (ii) Wurtz reaction. (iii) Sabatier and Senderen reaction. (iv) Frankland's synthesis.

(f) When ethyl iodide is gently heated with alcoholic caustic potash, it produces (i) methane. (ii) ethane. (iii) ethylene. (iv) acetylene.

Properties and Reactions of Hydrocarbons

3.1. PHYSICAL PROPERTIES OF HYDROCARBONS

(1) **Boiling point.** The first four alkanes are colourless gases. The next thirteen members (C_5H_{12} to $C_{17}H_{36}$) are colourless liquids. The higher alkanes are colourless solids. *The boiling points increase with rise of molecular mass* (see Fig.3.1.) Among the lower members, a difference of CH_2 corresponds to an increase of about 20 to 30° in the boiling points.

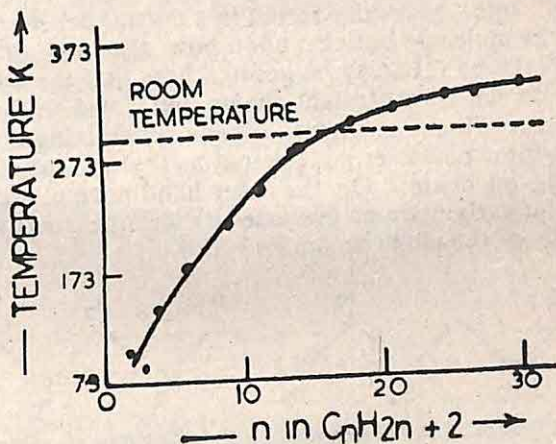


Fig. 3.1. Variation of boiling points of hydrocarbons.

We know that alkanes are non-polar compounds having weak van der Waal's forces of attraction between their molecules. These forces act along the surface of molecule and their magnitude increases with increase in surface area as well as with increase in polarisability. As the molecular size of alkane increases its surface area also increases which causes an increase in boiling point. It may be pointed out that isomeric forms of alkanes show small differences in their boiling points. *Generally, branched chain isomers have lesser boiling points than the corresponding normal isomers.* For instance, the boiling point of normal pentane and iso-pentane, are

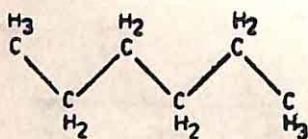
309 and 301K respectively. This is due to the fact that branched isomers are comparatively *more compact* and thus have lesser surface area than their normal counterparts. Such molecules having lesser surface area, therefore, possess lower boiling point since the van der Waal's forces of attraction operating between them are comparatively weaker.

Alkenes, alkynes, cycloalkanes and arenes also exhibit similar trends in their boiling points. However, unsaturated hydrocarbons possess somewhat higher boiling points than the corresponding saturated hydrocarbons due to *greater polarisability of their molecules*.

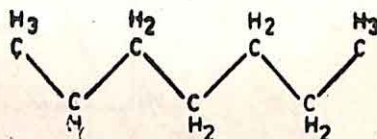
(2) **Melting points.** *The melting points of alkanes also increase with molecular size.* However, they do not show a very smooth gradation. The melting points of some members of normal alkanes are listed below.

Hydrocarbon	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
Melting point (K)	85.9	138	143.3	179	182.5	216.2

It can be noted from above that *the increase in melting point is much more in moving from an odd carbon atom containing alkane to the next higher alkane than in moving from an even carbon atom containing alkane to the next higher one.* This is due to the fact that the inter-molecular forces in a crystal depend not only on the size of the molecule but also upon how the molecules fit into the crystals lattices. It may be pointed here that the carbon atoms in alkanes do not form straight chains but form rather zig-zag type of chains. Thus, a normal alkane containing even number of carbon atoms possesses its terminal methyl groups on opposite side of the zig-zag chain. On the other hand normal alkane having odd number of carbon atoms possesses its terminal methyl groups on the same side of the chain as shown below.



n-HEXANE (EVEN NO. CARBON ATOMS)



n-HEPTANE (ODD NO. CARBON ATOMS)

†Terminal methyl groups on opposite side of zig-zag chain.)

(Terminal methyl groups on same side of zig-zag chain.)

Probably, alkanes having odd number of carbon atoms do not fit in so closely together in the crystal lattice as the alkanes having an even number of carbon atoms in their molecules. Consequently, lower energy is required to break the crystal structure of an alkane containing odd number of carbon atoms. This result in a slight rise in melting points in moving from an even number carbon containing alkane to the higher odd number alkane.

Alkenes and alkynes also exhibit more or less similar trends in their melting points. However, in case of alkenes, which exhibit geometrical isomerism, the less symmetrical *cis* isomer possesses lower melting point than the corresponding more symmetrical *trans* form. For instance, the melting points of *cis* 2-butene and *trans* 2-butene are 134.1 and 167.4K respectively. This is also due to the fact that the more symmetrical *trans* form fits better in the crystal lattice. In case of arenes the molecules having symmetrical structure have higher melting points. For instance, of the three xylenes (*o*-, *m*- and *p*-) the most symmetrical para isomer has the highest melting point.

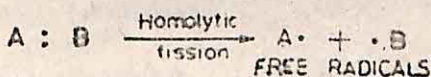
(3) Solubility. Since hydrocarbons are predominantly non-polar in character, so, they are soluble in non-polar solvents like carbon tetrachloride, ether, etc., but are insoluble in polar solvents like water. This is in line with the popular rule "like dissolves like". The liquid hydrocarbons themselves are good solvent for other non-polar substances.

(4) Density. In general, it can be stated that all hydrocarbons are lighter than water. The densities of alkanes as well as alkenes increase with increasing molecular masses, but becomes constant at about 0.8 g cm^{-3} .

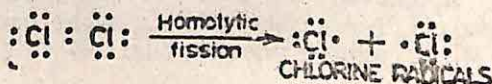
3.2. GENERAL NATURE OF ORGANIC REACTIONS

1. Type of bond fission. Organic reactions are not so simple and their reaction mechanism (i.e., the actual steps by which a reaction takes place) depends upon the nature of the covalent bonds. A covalent bond between two atoms, say A and B, of a compound A — B can be broken in two possible ways.

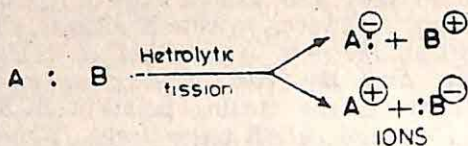
(i) *Homolytic fission* involves the breaking of a covalent bond so that each atom retains one of the two electrons of the shared pair.



These neutral entities (each atom or group of atoms) containing an odd or unpaired electron are highly reactive particles and they are known as *free radicals*. Free radicals are very short-lived and their high reactivity is due to their tendency to pair up the odd electron. The formation of these free radicals by homolytic fission may be illustrated below.

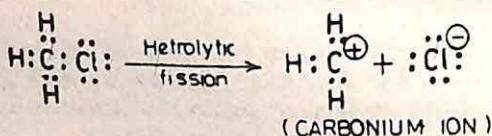


(ii) *Heterolytic fission* involves the breaking of a covalent bond in such a way that both shared pair of electrons are carried away by one of the atoms.



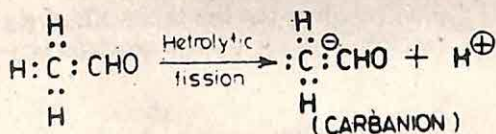
Thus, hetrolytic fission results in the formation of ions—one having a positive charge and the other a negative charge. The atom carrying away both shared electrons is called *anion*; while the other de arred of these shared electrons is called *cation*.

Very often the ionic species formed by hetrolytic fission bear a positive or negative charge on the carbon atom. Carbon atom carrying a positive charge is called *carbonium ion* and such an ion has only six electrons in the valency shell. For example,



Like free radical the carbonium ion is also very short-lived and highly reactive.

Carbon atom carrying a negative charge is called *carbanion* and such an ion contains eight electrons in its valency shell. For example,



Carbanions constitute important reaction intermediates in organic chemistry.

(2) **Nature of reagents.** The attacking reagents in a hetrolytic or ionic organic reactions are of two types.

(i) **Electrophilic reagent** is a reagent containing an atom which is "electron-deficient". Due to the presence of an electron density atom such a reagent attacks only at a centre of high electron density or carbanion. Consequently, an electrophilic reagent behaves as a Lewis acid. Some of the common electrophilic reagents are listed below :

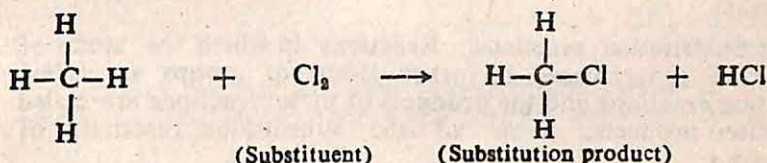
H^+ ; H_3O^+ ; NO_2^+ (from HNO_3) ; SO_2OH^+ (from H_2SO_4) ; NO^+ (from HNO_2) ; Br^+ (from Br_2) ; AlCl_3 ; FeCl_3 ; ZnCl_2 ; BF_3 ; $=\text{C}^+=\text{O}$; and CO_2 .

(ii) *Nucleophilic reagent* is an "electron-rich" reagent and possesses an unshared pair of electrons. Because of this free pair of electrons such a reagent attacks at a centre of low density or carbonium. Consequently, a nucleophilic reagent behaves as a Lewis base. It may be pointed out here that these reagents undergo only those reactions in which they can provide their unshared pair of electrons. Some of the important nucleophilic reagents are :

Cl^- ; Br^- ; I^- ; OH^- ; CN^- ; RO^- (alkoxide ion) ; $\text{R}-\text{C}^-$; $=\text{C}^-$; $>\text{O}^-$; $\equiv\text{N}$; NH_3 and RCOO^- (carboxylate ion).

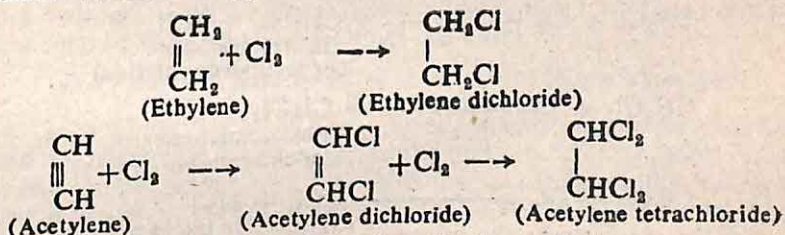
(3) *Types of reactions.* The organic reactions can be conveniently classified into following four categories.

(i) *Substitution reaction* involves the direct replacement of a hydrogen atom or some other group of a molecule by other atom or group without causing any basic change in the structure of the remaining part of the molecule. The new atom or group which enters the molecule is known as "substituent" and the product so formed is known as "substitution product". For example ;

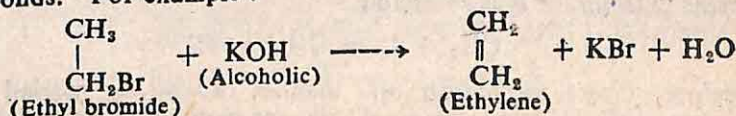


The substitution reaction may be an electrophilic or nucleophilic type depending upon whether the attacking reagent is electrophilic or nucleophilic in nature. The electrophilic substitution reactions are generally represented as SE ; while the nucleophilic substitution reactions are represented as SN.

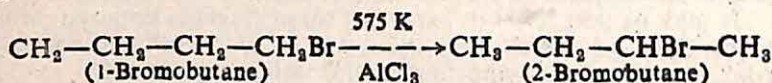
(ii) *Addition reaction* involves the formation of a product by the combination of two or more reacting substances. It may be pointed that in addition reactions one of the reactants always contain a double or tripple bond in its molecule. For example :



(iii) *Elimination reaction* involves the loss of atoms or groups of atoms from a molecule yielding compounds containing double or triple bonds. For example :



(iv) *Rearrangement reaction* involves either the migration of a functional group from one atom to another or complete rearrangement of the carbon atom chain to form a new product. For example :

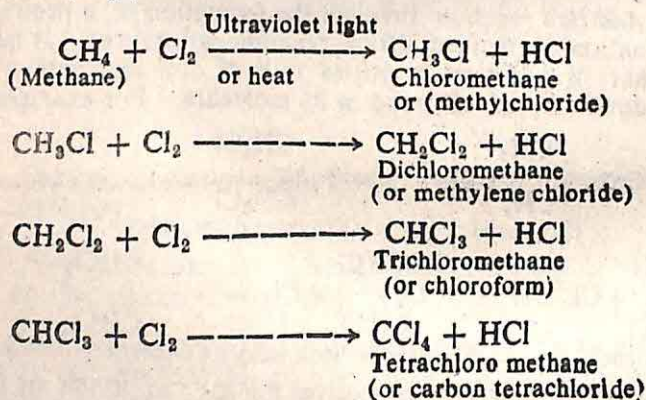


3.3. CHEMICAL PROPERTIES OF ALKANES

Alkanes are non-polar molecules containing only strong, sigma type single bonds between carbon-carbon and carbon-hydrogen atoms. Consequently, they are a rather "unreactive class of compounds." They are quite inert towards, common reagents (such as acids, alkalis, oxidising or reducing agents, etc.) under ordinary conditions. Their name paraffin (parum=little : affinis=affinity) originated from this inertness. Under strong conditions, however, alkanes do undergo a few reactions most of which are of substitution type. The more important reactions of alkanes are described below.

(1) **Substitution reactions.** Reactions in which the atoms of a compound are replaced by other atoms or groups are called substitution reactions and the products of these reactions are called substitution products. Some of the substitution reactions of alkanes are :

(a) *Halogenation.* When alkanes react with halogen (chlorine or bromine) in the presence of diffuse sunlight or ultraviolet light or at higher temperature (520–670K) or in presence of a halogen carrier (like iron) the H atoms of alkanes are successively replaced by halogen atoms, e.g.,



The reaction of alkanes with fluorine is explosive and violent ; whereas with iodine it is reversible.



Therefore, direct iodination of alkanes cannot be carried out. However, iodination reaction of alkanes may be brought about in presence of an oxidising agent (such as iodic acid, nitric acid, etc.)

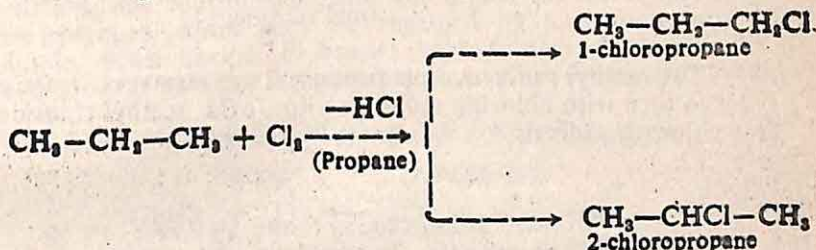
which converts the hydroiodic acid into iodine thereby checking the backward reaction.



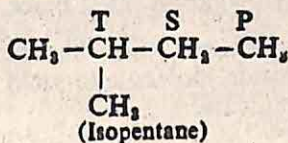
From the above it is clear that the order of reactivity of halogens towards alkane is,

Flourine > Chlorine > Bromine > Iodine

Halogenation of higher hydrocarbons yield a mixture of all possible isomeric halogen derivatives. For instance, propane on chlorination gives a mixture of 1-chloropropane and 2-chloropropane.



It may be pointed here that different classes of hydrogen atoms (i.e., tertiary, secondary and primary hydrogen atoms).



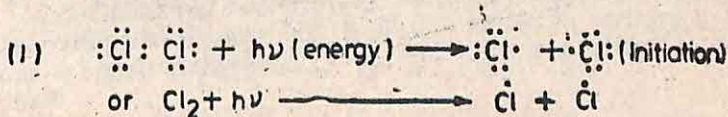
can be substituted in the following order.

Tertiary > Secondary > Primary

Thus, in case of isopentane the extent of substitution to 2-chloropropane is greater than 1-chloropropane in the mixture of the two since the former involves a secondary hydrogen atom and it is formed with greater ease than the latter.

Mechanism of halogenation involves the following stages :

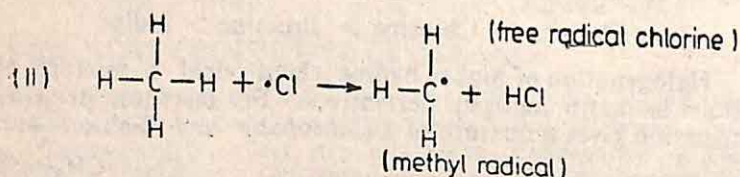
(i) *Chain initiation step.* Since the reaction between methane and chlorine takes place either in the presence of ultraviolet light at room temperature or in dark at 520K, it is believed that halogenation is initiated by the homolytic fission of the chlorine molecules into chlorine atoms. The 243 kJ mol⁻¹ of energy, required for this step is supplied by ultraviolet light or by heat.



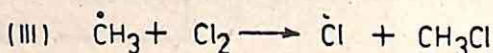
Chlorine free radicals

The chlorine atom obtained by this process has an odd electron and is called free radical. Such radicals are highly reactive.

(ii) *Chain propagation step.* Chlorine atoms collide with molecules of methane thereby removing a hydrogen atom from the latter forming hydrochloric acid molecule and methyl free radical.

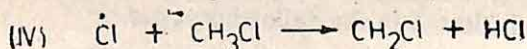


The methyl radicals, thus produced, are also very reactive and react in turn with chlorine molecules to form methyl chloride and free chlorine radicals.

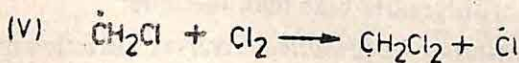


Thus, in steps (ii) and (iii) one free radical is used up and another is formed. So, the steps (ii) and (iii) are repeated several times, thereby chain propagation takes place.

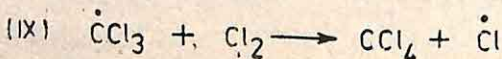
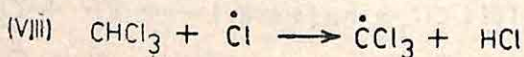
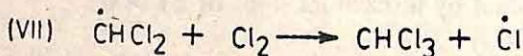
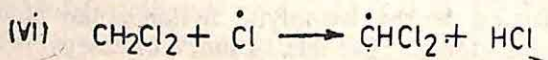
As the reaction proceeds the chlorine free radical can also react with methyl chloride molecule to yield hydrogen chloride and a substituted methyl radicals.



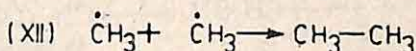
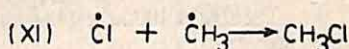
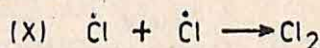
The substituted methyl radical, thus, produced reacts with another molecule of chlorine to form methylene dichloride and chlorine radical.



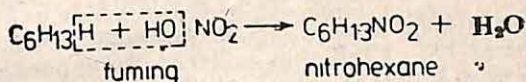
The process may extend further till all the hydrogen atoms are substituted leading to the formation of carbon tetrachloride.



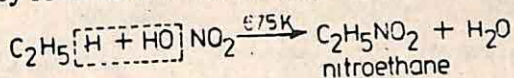
(iii) *Chain termination step.* The above chain reactions do not continue indefinitely and certain reactions called chain termination steps remove free radicals by combining amongst themselves without giving rise to any new radical *e.g.*,



(b) *Nitration.* Nitric acid has no action on lower alkanes but by its long and continued action on higher hydrocarbons one of their hydrogen atoms may be replaced by a nitro group. For example, when hexane is heated with fuming nitric acid for 48 hours about 10% of the hydrocarbon is converted into nitrohexane.

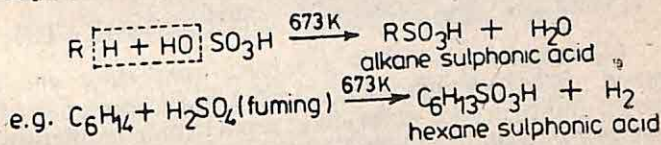


More recently, the "vapour-phase nitration process" have been developed for nitration of alkanes except methane. For example, when ethane is mixed with nitric acid vapours and heated to 675K, they react to form nitroethane.



Since the above reaction is carried out at high temperatures, so, some of the C—C linkages are attacked thereby resulting in the formation of simpler nitro compounds also. Thus, in the above case some nitromethane (CH_3NO_2) is also produced along with nitro ethane.

(c) *Sulphonation.* Higher alkanes, from hexane onwards, react with fuming sulphuric acid at high temperatures to form alkane sulphonic acid.

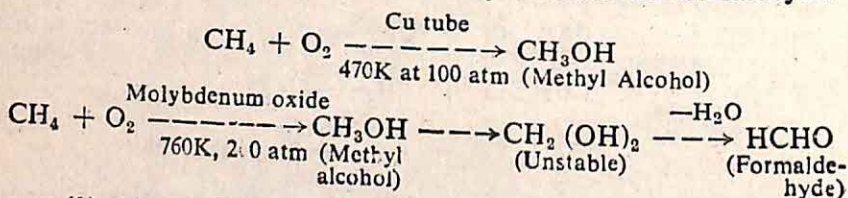


It may be pointed out here that primary alkanes undergo sulphonation readily; while the secondary and tertiary ones do not sulphonate under equivalent conditions.

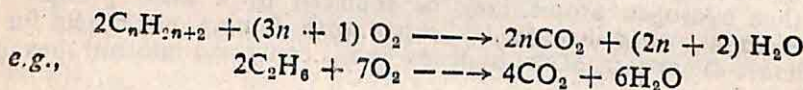
(2) *Oxidation.* (a) Normal alkanes are not oxidised by potassium permanganate but the latter oxidises a tertiary hydrogen atom to a hydroxyl group. Thus, isobutane is oxidised to tertiary butanol.



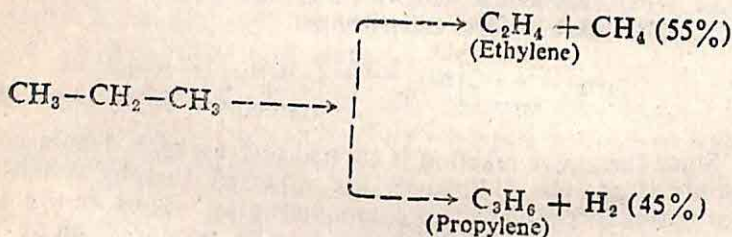
However, normal alkanes may be oxidised under suitable condition (in presence of a catalyst, high temperature and pressure) to alcohols and aldehydes. For example, catalytic oxidation of methane leads to the formation of methyl alcohol and formaldehyde.



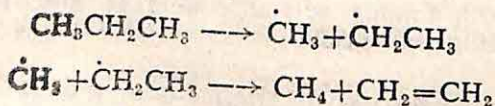
(b) Alkanes burn in air or oxygen to form carbon dioxide and water.



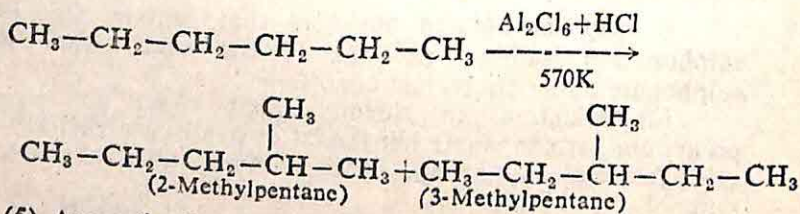
(3) **Pyrolysis (cracking).** When the alkanes are passed through tubes heated to 770–875K they undergo decomposition or cracking. The nature of products so obtained depends on the structure of alkane, presence of a catalyst and pressure under which cracking is carried out. For example, propane decomposes at 735K as follows:



The cracking process is believed to proceed by a free radical mechanism as shown below.



(4) **Isomerisation** is the process of converting one isomer into another. When *n*-alkanes are heated in the presence of aluminium chloride and hydrogen chloride at a particular temperature, they are converted into branched-chain isomers, e.g.,

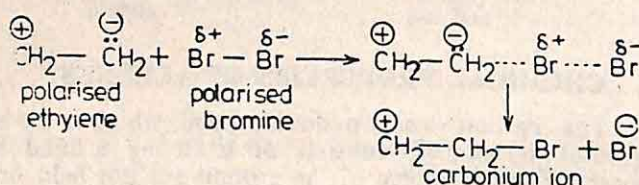


(5) **Aromatisation.** When alkanes containing six or more carbon atoms are heated under pressure and presence of a catalyst

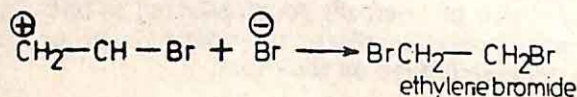
Mechanism. A halogen molecule is non-polar. However, in the vicinity of a dense electron cloud of carbon carbon double bond it gets polarised, i.e.,



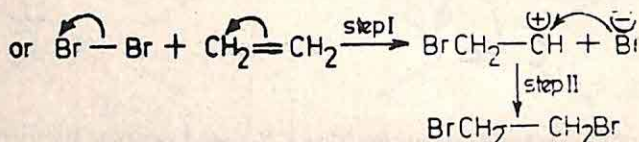
This polarised molecule approaches the ethylene molecule forming a transition complex which subsequently breaks as shown below.



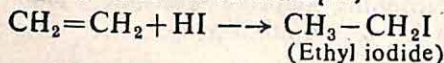
The bromide ion so formed then attaches to the positively charged carbon atom to form addition product, ethylene bromide.



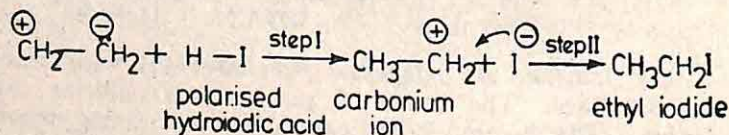
The above mechanism may be represented in brief as follows.



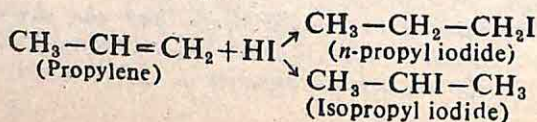
(3) **Addition of halogen acids.** All halogen acids (HCl, HBr, HI) readily add to alkenes forming alkyl halides. The order of reactivity is $\text{HI} > \text{HBr} > \text{HCl}$. For example,



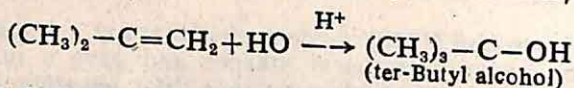
Mechanism. The addition of halogen acids is also a two step ionic process. For example, the addition of HI to ethylene is shown below.



In case of unsymmetrical alkenes the addition of halogen acid (or any other reagent consisting of two different atoms or groups) can result in the formation of two different isomeric products. For example,

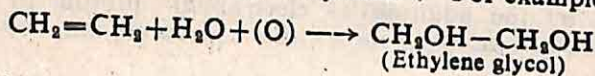


(5) *Addition of water.* The more reactive alkenes add on water in the presence of dilute acids to yield alcohols, e.g.,



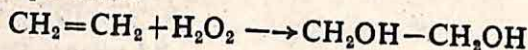
(B) *Oxidation of alkenes.* Alkenes are readily oxidised forming different products depending upon the nature of oxidising agent used.

(1) *With potassium permanganate.* Alkenes on treatment with cold, dilute, slightly alkaline or neutral solution of potassium permanganate are oxidised to dihydroxy compounds called glycols. This reaction is known as "hydroxylation". For example :

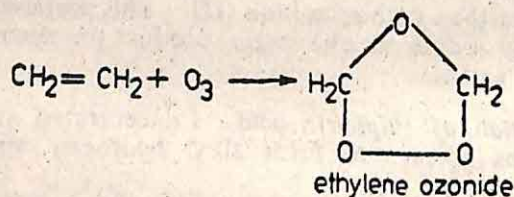


This reaction is used as a test for unsaturation in a compound since potassium permanganate solution gets decolourised (Baeyer's test).

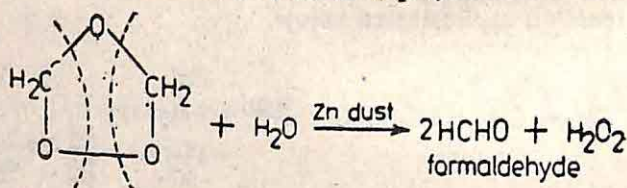
The hydroxylation reaction can also be brought about by using hydrogen peroxide.



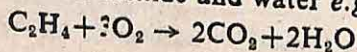
(2) *With ozone.* When ozone is passed through a solution of alkenes in an inert solvent the latter gets oxidised forming ozonide. This reaction is known as "ozonolysis." For example,



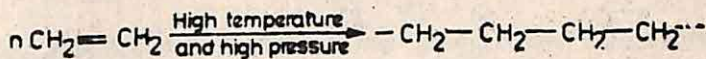
The ozonides on treatment with water in presence of zinc dust undergo decomposition yielding aldehydes or ketones depending upon the nature of ozonides. For example,



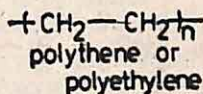
(3) *Combustion.* Alkenes burn in air or oxygen with a luminous flame producing carbon dioxide and water e.g.,



(C) *Polymerisation.* Alkenes polymerises in presence of suitable catalysis, e.g.,



or



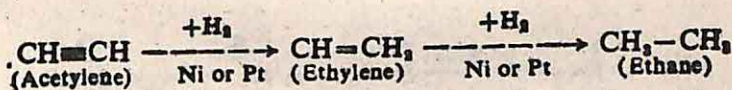
Such a process in which a large number of molecules of a compound react additively to form bigger molecules (called polymers) is known as "polymerisation."

3.5. REACTIONS OF ALKYNES

Alkynes contain a carbon-carbon triple bond which is made of a strong σ -bond and two weak π -bonds. A triple bond may be considered to be equivalent to two double bonds and consequently alkynes are more reactive than alkenes. The alkynes, thus, readily undergo addition reactions, the majority of which involves electrophilic addition. The important reactions of alkynes are discussed below.

(A) *Electrophilic addition reactions.* Like alkenes, alkynes also forms addition products.

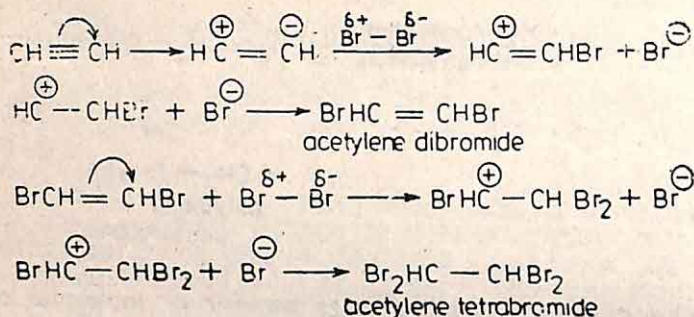
(1) *Addition of hydrogen.* In presence of a suitable catalyst, alkyne can add on hydrogen to form alkenes and ultimately alkanes, e.g.,



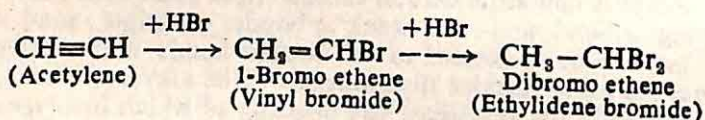
(2) *Addition of halogens.* Chlorine and bromine adds on to alkynes to form di-and tetrahalides. For example :



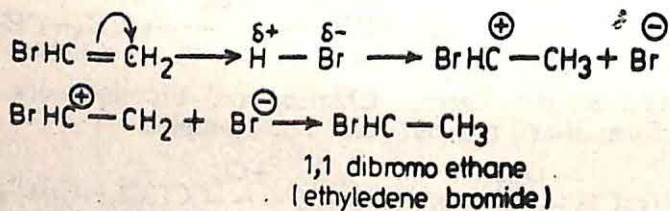
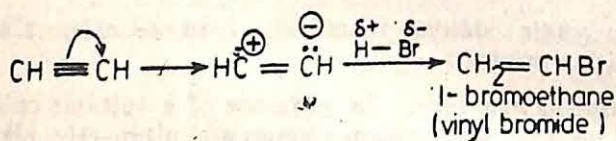
The mechanism involved is of electrophilic type (as in the case of alkenes) as shown below :



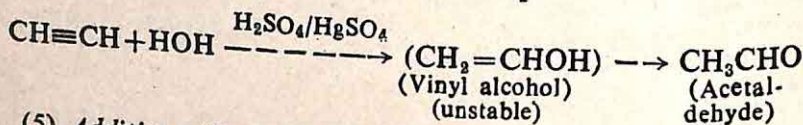
(3) *Addition of halogen acids.* Alkynes add on one or two molecules of halogen acids in accordance with Markownikoff's rule yielding mono and dihalogen derivatives of alkene and alkane respectively. For example :



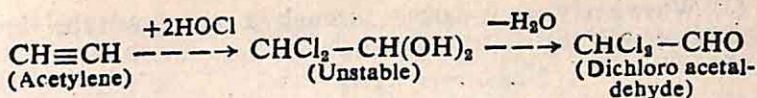
The mechanism of reaction is :



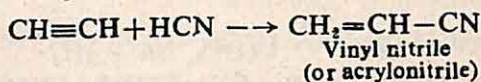
(4) *Addition of water.* Water in presence of dilute sulphuric acid and mercuric sulphate, adds on to alkynes forming carbonyl compounds, aldehydes or ketones. For example :



(5) *Addition of hypochlorous acid.* Alkynes add on two molecules of hypochlorous or hypobromous acid to yield dihaloaldehydes or ketones. For example,

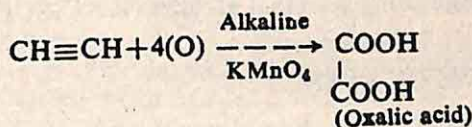
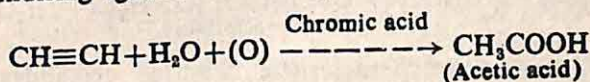


(6) *Addition of hydrogen cyanide.* Alkynes react with hydrogen cyanide to form vinyl nitrile. For example :

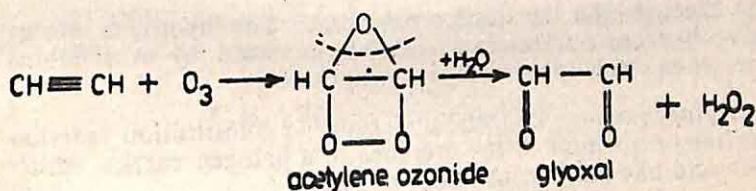


(B) *Oxidation of alkynes.* Alkynes are readily oxidised forming different products depending upon the nature of oxidising agent used.

(1) *With potassium permanganate.* Alkynes on oxidation with potassium permanganate or chromic acid yield carboxylic acids. However, the nature of acids obtained may be different in the case of two oxidising agents. For example :



(2) *With ozone.* When ozone is passed through a solution of alkynes in an inert solvent, the latter gets oxidised forming ozonide. The ozonide on hydrolysis gives dicarbonyl compounds. For example,



(3) *Combustion.* Alkynes burn in air or oxygen with a luminous flame producing carbon dioxide and water.



The reaction is "highly exothermic" yielding approximately 1248 kJ per mole of heat and produces a flame temperature of more than 3000K.

(C) *Polymerisation.* (1) When acetylene is passed into a solution of cuprous chloride and ammonium chloride in hydrochloric acid, vinyl acetylene is formed.

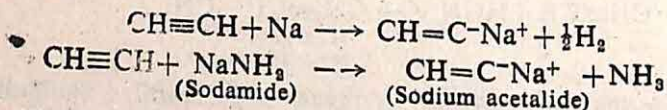


3.54 | ESSENTIALS OF CHEMISTRY

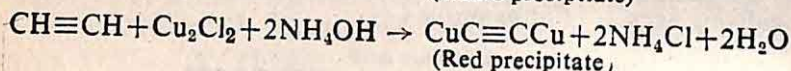
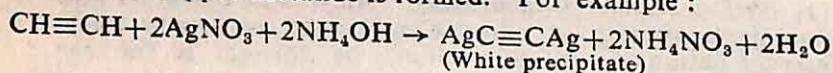
(2) When acetylene is passed through a red hot tube three molecules join together to form benzene.



(D) Formation of acetalides. (1) Alkynes react with alkali metals and sodamide to form salts known as acetalides. For example,



(2) When alkynes are passed through ammoniacal solutions of silver nitrate or copper sulphate, characteristic precipitates of silver acetalide or copper acetalide is formed. For example :



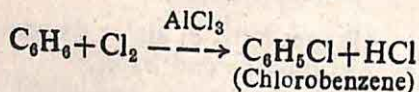
The formation of these characteristic coloured acetalides can be used for distinguishing terminal alkynes ($\text{R}-\text{C}\equiv\text{CH}$) from other hydrocarbons.

3.6. REACTIONS OF ARENES

Arene (benzene and its homologues) possesses a six carbon atom ring with an alternate system of double and single bonds. This ring is quite stable and hence it does not readily give the addition reactions of the unsaturated compounds. However, they easily undergo a number of substitution reactions. The important reactions of arenes are discussed below with reference to benzene.

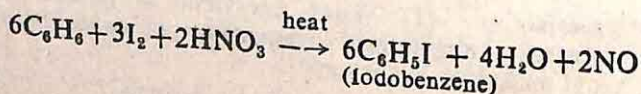
(A) Electrophilic substitution reactions. The hydrogen atoms attached to benzene nucleus can readily be replaced by other atoms or groups when electrophilic reagents attack on it.

(i) *Halogenation.* Benzene undergoes a substitution reaction with chlorine or bromine in the presence of a halogen carrier, which is a Lewis acid like anhydrous AlCl_3 or FeCl_3 .

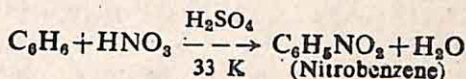


In this reaction iron can also be used as a catalyst, since it gets converted into FeCl_3 by reacting with chlorine.

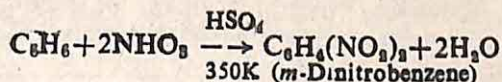
Direct iodination takes place in presence of oxidising agents like iodic acid or nitric acid.



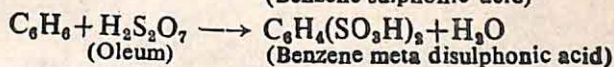
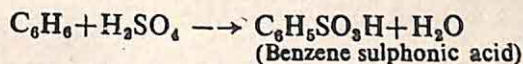
(ii) *Nitration*. When benzene is treated with a mixture of concentrated nitric and sulphuric acids at about 330K, nitrobenzene is obtained.



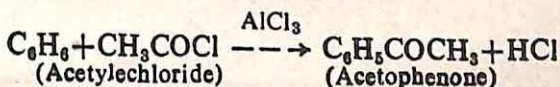
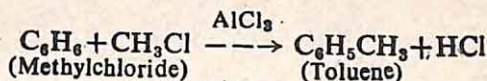
If a temperature of about 350K is used dinitrobenzene is obtained.



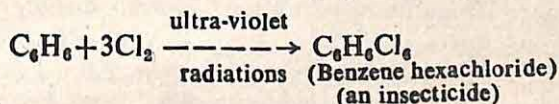
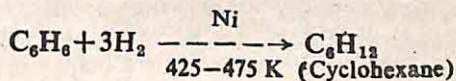
(iii) *Sulphonation*. When benzene is heated with concentrated sulphuric acid, benzene sulphonic acid is produced. However, with oleum (fuming sulphuric acid) the product is benzene meta-disulphonic acid.



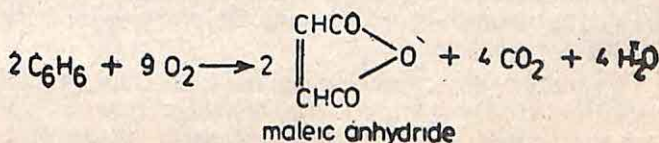
(iv) *Friedel-Craft's reaction*. Benzene reacts with reagents like alkyl halides, acetyl chloride, etc., in presence of anhydrous AlCl_3 to yield a wide variety of compounds. For example :



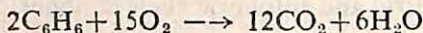
(2) *Addition reaction*. Benzene (and its homologues) undergo some addition reactions under drastic conditions. For example ;



(3) *Oxidation*. Under normal conditions benzene is quite stable towards oxidising agents. However, when a mixture of air and benzene vapours is passed over vanadium pentoxide catalyst at 775K it yields maleic anhydride.

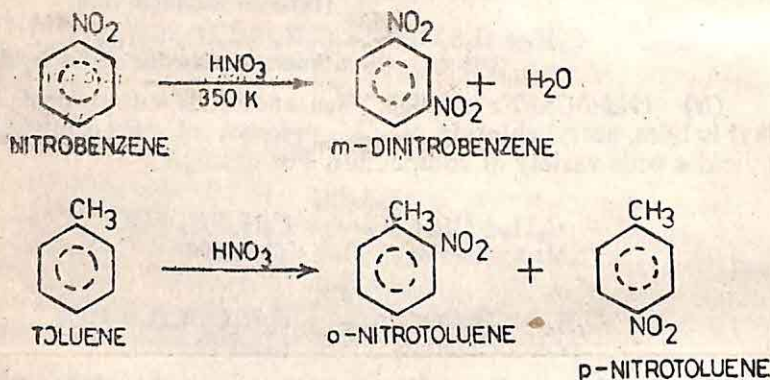


(4) Combustion. They burn with a sooty flame giving CO_2 and H_2O , e.g.,



3.7. ORIENTING INFLUENCE OR DISUBSTITUTION OF BENZENE

The six hydrogen atoms of benzene molecule are equivalent. Consequently, the replacement of any one hydrogen atom of benzene ring with another group does not lead to any isomeric products. However, the replacement of second hydrogen atom leads to isomeric disubstituted products. These disubstituted isomeric products are ortho (1 : 3); meta (1 : 2) and para (1 : 4). It has been found that the type of disubstitution products formed depends on the nature of the first group already present in the ring. Thus, if nitrobenzene is further nitrated the second nitro group will go into the ring mainly in the meta position. On the other hand, when toluene is nitrated a mixture of ortho and para nitro toluene is formed.



Consequently, nitro group is *m*-directing; while methyl group is *ortho* and *para* directing. Thus, the group already present in the nucleus of benzene has a directive or orienting influence on the position of the new substituent in the benzene ring. Each group is found to direct mainly to either *meta* or *ortho* and *para* positions.

On the basis of their directive influence the groups present in mono substituted benzene ring are classified as *ortho* and *para* directing or *meta* directing groups as given below :

(i) *Ortho-para directing groups* are $-\text{CH}_3$ (methyl); $-\text{C}_2\text{H}_5$ (ethyl); $-\text{OH}$ (hydroxy); $-\text{NH}_2$ (amino); $-\text{Cl}$ (chloride); $-\text{Br}$ (bromide); and $-\text{I}$ (iodide).

(ii) *Meta directing groups* are $-\text{NO}_2$ (nitro); $-\text{SO}_3\text{H}$ (sulphonic); $-\text{CN}$ (cyanide); $-\text{CHO}$ (aldehydic); $-\text{COR}$ (ketonic); and $-\text{COOH}$ (carboxylic).

A number of empirical rules have been formulated to predict the position of new entrant in the benzene nucleus. Of these Crum-Brown and Gibson rule is very satisfactory. According to it "if a substituent *X* already present in the nucleus is such that its hydrogen compound *HX* can be easily and directly oxidised to its hydroxy

compound (HOX), it directs the newly entering group to the meta position, otherwise in the ortho and para position." For example, CHO group forms with hydrogen the compound HCHO, which can be easily and directly oxidised to HCOOH; hence, -CHO group is meta directing. Similarly, -NO₂ group with hydrogen forms HNO₂, which is readily oxidised to HNO₃, hence -NO₂ is also meta directing. On the other hand -NH₂ group forms NH₃, which can not be easily oxidised, so -NH₂ group is ortho and para directing. Other example are given below:

Group X	Compound with hydrogen, HX	Can HX be directly and easily oxidised to HOX or not	Directive influence
CH ₃ Cl	CH ₃ Cl	No	Ortho and para.
OH	H ₂ O	No	Ortho and para.
SO ₃ H	H ₂ SO ₃	Yes, to H ₂ SO ₄	Meta.
Cl	HCl	No	Ortho and para.
CN	HCN	Yes, to HCNO	Meta.

QUESTIONS

(A) Essay Type :

1. Describe the physical properties of hydrocarbons with a particular reference to boiling points and melting points.

2. What is meant by homolytic and heterolytic fission? Explain with examples, the formation of free radicals, carbonium ions and carbanions.

3. What are electrophilic and nucleophilic reagents? Which of the two, you think would readily attack a carbonium ion and why?

4. Define and give examples of the following reactions: (i) Addition reaction, (ii) substitution reaction, (iii) elimination reaction, (iv) rearrangement reaction.

5. Describe the chemical properties of alkanes with particular reference to (i) halogenation reaction, (ii) nitration reaction, (iii) sulphonation reaction and (iv) oxidation reaction.

6. Write notes on: (i) isomerisation, (ii) pyrolysis and (iii) aromatisation.

7. Describe the chemical properties of alkenes with particular reference to: (i) halogenation reaction, (ii) sulphonation reaction, and (iii) oxidation reaction.

8. What is Markownikoff's rule? How will you justify it on theoretical basis.

9. Describe the chemical properties of alkynes with particular reference to: (i) addition of hydrogen, (ii) addition of halogens, (iii) addition of halogen acids, and (iv) oxidation.

10. Describe in detail the electrophile substitution reactions of arenes.

11. State Crum-Brown and Gibson rule. How does this rule help an investigator in locating the position of nitro group in the nucleus when the group is introduced in (i) nitro benzene and (ii) toluene.

(B) Short-Answer Type :

12. Why the boiling points of branched chain alkanes are lower than their normal isomers ?

13. Why alkanes containing odd number of carbon atoms have lower melting points than expected value ?

14. Why the boiling points of alkenes go on increasing as we proceed from 1-propene to 1-heptene ?

15. What is the directive influence of (i) an electron-releasing group ; (ii) an electron-withdrawing group ?

16. In an electrophilic substitution why does OH group direct the newly entering group in ortho and para position ?

17. In an electrophilic substitution reaction why does NO_2 group direct the newly entering group in the meta position.

18. List at least five electrophilic reagents.

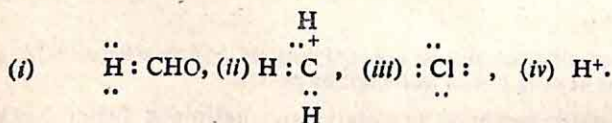
19. List at least five nucleophilic reagents.

(C) Objective Type

20. Put a mark for the correct answer.

(a) The boiling points of alkanes increase with rise of molecular mass. Among the lower members, a difference of CH_2 corresponds to an increase of about (i) 20 to 30°, (ii) 2 to 4°, (iii) 5 to 10°, (iv) 10 to 20°.

(b) Which one of the following is a carbanion ?



(c) Which one of the following is an electrophilic reagent : (i) H^+ , (ii) =N , (iii) NH_3 , (iv) Cl^- .

(d) The reaction product of ethylene and ozone upon hydrolysis gives, (i) formaldehyde, (ii) formic acid, (iii) acetaldehyde, (iv) acetic acid.

(e) Acetylene reacts with sulphuric acid in presence of 1% mercuric sulphate to produce a compound known as (i) oxalic acid, (ii) formic acid, (iii) acetaldehyde, (iv) ethylene glycol.

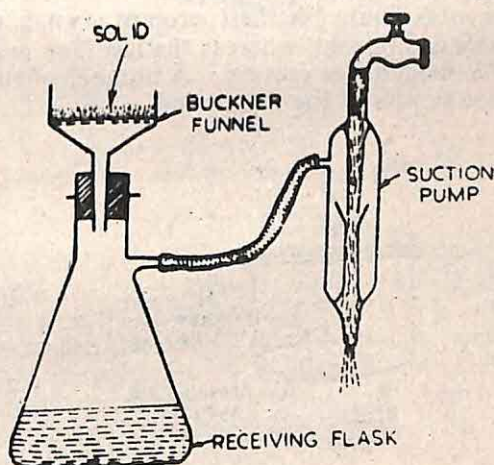
(f) Benzene reacts with concentrated nitric acid in presence of concentrated sulphuric acid to give (i) nitro benzene, (ii) dinitrobenzene, (iii) trinitrobenzene, (iv) s-trinitrobenzene.

Purification and Characterization of Organic Compounds

4.1. PURIFICATION OF ORGANIC COMPOUNDS

Organic compounds isolated either from natural source or prepared by synthetic methods are generally associated with a number of impurities of various nature. Before submitting the compound to diagnosis it is essential to obtain that in pure state (*i.e.*, free from impurities). Various methods frequently employed for separation and purification are enumerated below.

(1) **Filtration.** This process is frequently employed for the separation of insoluble solid impurities from a liquid substance. Quick filtration may be effected with the aid of a Buchner funnel and a suction pump (*see* Fig. 4.1). Still more rapid filtration can be effected by electric centrifuge.



[Fig. 4.1. Use of Buchner funnel.

(2) **Crystallization.** This technique is used for separating or purifying a solid substance which is soluble in some solvent like water, alcohol, ether, benzene, chloroform, carbon tetrachloride,

pyridine, acetone, etc. The efficiency of process depends mainly upon the choice of suitable solvents. A good solvent is one which dissolve a large amount of the substance at an elevated temperature and deposits the same on cooling. Since most of the solvents are highly inflammable; consequently their use require a great care.

Procedure. A hot saturated solution of the substance in a suitably selected solvent is allowed to filter hot, thereby undissolved impurities are left on the filter bed. Funnel surrounded with hot water jacket is employed to prevent crystallization during the course of filtration (See Fig. 4.2). The filtered solution is allowed to cool slowly when crystals of purer variety are obtained leaving behind impurities in the mother liquor. The crystals are then separated by filtration and subsequently dried in a vacuum desiccator Fig. 4.3. Crystallized crop is redissolved in minimum quantity of fresh solvent and process of crystallization is repeated until the solid melt at the same sharp temperature on two successive crystallization.

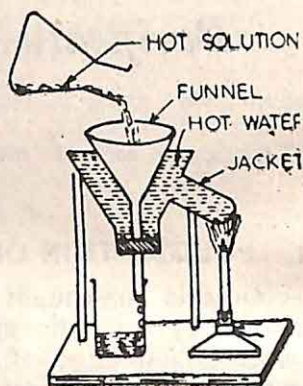


Fig. 4.2. Hot water funnel.

(3) **Fractional crystallization.** In case the compound and the contaminated impurities do not differ much in their solubilities, then separation can be effected by fractional crystallization. On cooling the hot saturated solution, the least soluble component separates out first leaving behind liquor which will be rich in more soluble components. Thus, the first crop of crystals will be richer to the least soluble component; whereas the last one will be richer in most soluble component present. A number of such repetition will afford a pure sample of the compound.

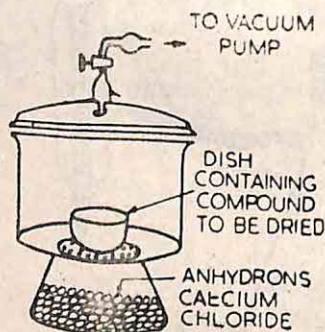


Fig. 4.3 Use of vacuum desiccator for drying.

(4) **Sublimation.** Large number of organic substances (like camphor, naphthalene, anthracene, indigo, anthraquinones, benzoic

acid etc.) vaporize directly to gaseous state when heated without undergoing liquefaction and vice versa on cooling, and hence they can be best purified from non-volatile impurities by sublimation technique.

The crude sample of the substance is placed on a watch glass or shallow porcelain basin covered with a small inverted funnel, the stem of latter is packed with cotton or glass-wool. The basin is carefully heated on a sand bath when pure solid sublimate gets deposited on the inner walls of the funnel, while the non-volatile impurities are left behind as residue in the basin. Substances which undergo decomposition when sublimed at ordinary pressure are sublimed under reduced pressure.

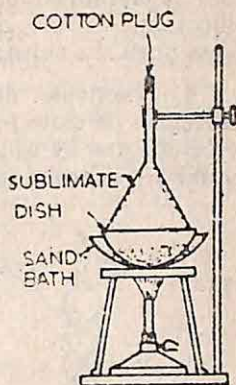


Fig. 4.4. Sublimation.

(5) **Simple distillation** Purification of a volatile liquid contaminated with non-volatile impurities is effected by this technique in which the substance is transferred into gaseous state and condensed to liquid or solid state at another place. In case the boiling points of components are fairly apart, their separation in pure state can be effected by a single distillation operation.

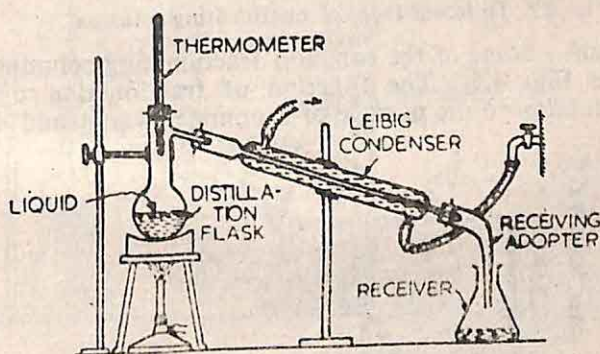


Fig. 4.5. Simple distillation,

The operation is carried out in a distillation flask (containing the crude sample to be purified) fitted with a thermometer, a condenser and a receiver as depicted in Fig 4.5. The distillation flask is heated and when the boiling point of most volatile component is reached, the same begins to distil over practically in pure state. The temperature remains steady till this constituent passes over and then the temperature begins to rise until the boiling point of next higher boiling component is reached and the same begins to distil over and so on. Bumping and superheating of the liquid may be avoided by adding a few small pieces of glass beads of unglazed porcelain to the flask.

In case the boiling point of liquid is above 390K an air condenser (a long wide glass tube attached to the distillation flask)

should be employed in place of a Leibig water condenser. Further purification of the distillate can be achieved by repeating this process until the substance distils over at its boiling point.

(6) **Fractional distillation.** If the boiling points of volatile constituents lie close together, a more efficient separation of these may be effected by using a fractionating column in which the mixed vapours are exposed to a large cooled surface before they enter the

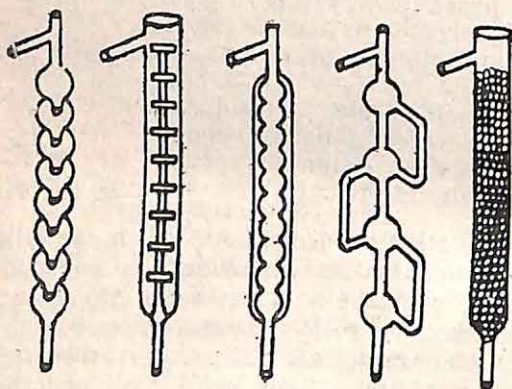


Fig. 4.6. Different types of fractionating columns

condenser itself. Some of the common fractionating columns used are shown in Fig. 4.6. The function of fractionating column is to cause obstruction to the passage of vapours upwards and liquids downwards.

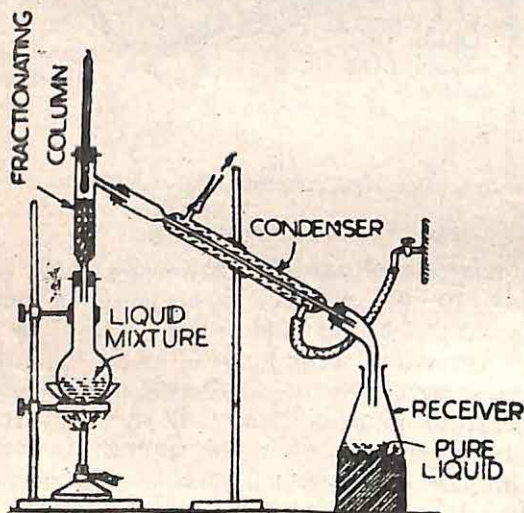


Fig. 4.7. Fractional distillation

Suppose the sample contains volatile components A and B of which former is more volatile (*i.e.*, of lower boiling point). The liquid mixture is placed in a distillation flask fitted with a fraction-

ating column, a thermometer and a condenser as shown in Fig. 4.7. On heating the flask the upcoming vapours contain a greater proportion of A than does the original mixture. The ascending vapours are partially cooled and the less volatile constituent B condenses more rapidly than A. The condensate moves down, and as it meets the fresh upcoming vapours it scrubs them thereby causing the condensation of their less volatile constituent B. Thus, at each obstruction there occurs an exchange of constituents between ascending vapours and descending liquid; and as the vapours ascend higher and higher it becomes more rich in low boiling constituent A, and the vapours escaping the fractionating column consist almost exclusively of A; while the condensed liquid flowing back into the distillation flask is rich in B. For getting more pure sample the process can be repeated separately with the distillate and the liquid left in the distillation flask. Longer is the fractionating column more perfect is the separation.

(7) **Vacuum distillation.** In case the liquids decompose at or below their boiling point under ordinary pressure, purification can not be effected by ordinary distillation process. However, in such cases the distillation is best carried under reduced pressure, since the use of reduced pressure lowers the boiling point thereby the decomposition is prevented. For example, glycerine boils at 563K

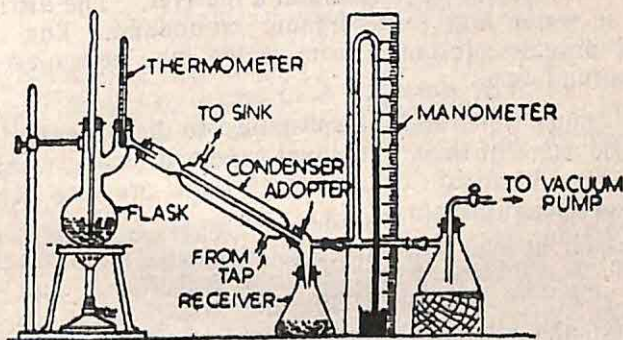


Fig. 4.8. Vacuum distillation.

with decomposition under 760 mm pressure, but distils over undecomposed at 453K under a pressure of 12 mm. Specially designed arrangement for distillation under reduced pressure is shown in Fig. 4.8.

Note. All joints and connections must be perfectly airtight before vacuum distillation is carried out.

(8) **Steam distillation.** Many organic liquids and solids, which are practically immiscible with water, prove to be very volatile in a current of steam and may easily be purified or separated in this way provided the other components are non-volatile under these conditions. Practical example of this technique is the isolation of most of essential oils like rose oil from flowers, separation of isomers e.g., *c*-nitrophenol (volatile in steam) from

p-nitrophenol (non-volatile). Suitable arrangements for steam distillation is shown in Fig. 49.

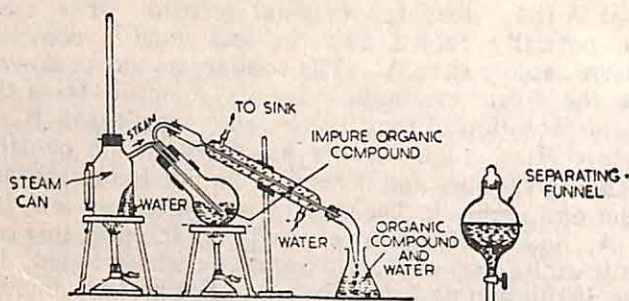


Fig. 49. Steam distillation.

A vigorous current of steam from a generator (a tin can or flask provided with a cork carrying a long safety tube reaching nearly to bottom and with a side delivery tube) is passed into a flask containing the impure organic substance and water, which is heated from below. This flask is kept inclined so as to avoid splashing of its contents and to provide assistance in mechanical carrying over of the substance into the condenser. The volatile matter along with steam is collected in a receiver. The distillate will consist of water and pure organic compound. The final separation of organic substance from water may be achieved by using a separating funnel.

Theory. Since water and the substance to be separated are immiscible, the sum of their individual vapour pressure, when the mixture boils, must be equal to the atmospheric pressure p . (By Dalton's law of partial pressures), i.e.,

$$p = p_1 + p_2$$

or

$$p_2 = p - p_1$$

Evidently, the partial vapour pressure of each constituent is less than the atmospheric pressure and hence the apparent boiling point of each constituent is less than normal boiling point. Consequently, the principle involved in steam distillation process is somewhat similar to that in vacuum distillation.

Let the rate at which the organic substance and water distils over be W_1 and W_2 respectively. Let M be the molecular mass of the organic substance and the molecular mass of water $m = 18$. then, we have

$$\frac{W_1}{W_2} = \frac{p_1 \times 18}{p_2 \times M} = \frac{p_1 \times 18}{(p - p_1)M}$$

The value of p and p_1 are calculated from the standard tables and barometric height respectively and hence the ratio of the masses of water and organic substance in the distillate may be computed.

(9) **Differential extraction.** Organic compound, whether solid or liquid, can be recovered from its aqueous solution by shaking it in a separating funnel with a suitable water immiscible solvent in which the organic compound is much more soluble than in water. The separating funnel is then allowed to stand undisturbed for sometime when solvent (containing most of the compound)

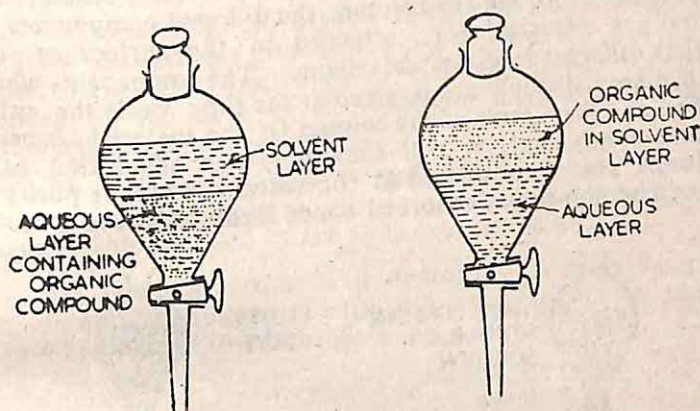


Fig. 4.10. Differential extraction.

and water form two separate layers (see Fig. 4.10). The solvent layer is then separated from aqueous layer by opening the tap and subsequently evaporated to get the organic compound. This method is normally used for recovering non volatile organic compounds.

(10) **Chromatography.** In 1906 the botanist M. Tswett described how coloured plant pigments (such as chlorophyll) could be separated into components of different hues (colours) by passing a solution of the pigment through a column of finely divided adsorptive material such as precipitated chalk (CaCO_3). The method was called chromatography. "Chromatography", as understood today, may be defined as the process of selective retardation of one or more components of a fluid uniformly percolating through capillary passage ways. It is based on the difference in the rates at which the components of a mixture move through a porous medium (called, the stationary phase) under the influence of some solvent or gas (called, the moving phase).

Chromatography is an extremely valuable method for the separation of ionic and molecular species, non-polar and polar molecules, geometrical and optical isomers, isotopes, etc. It has also been used for the identification and purification of the constituents of a mixture. Chromatographic techniques may be classified into (a) column chromatography, (b) paper chromatography, (c) gas chromatography, (d) ion exchange chromatography, etc.

The simplest chromatographic method is *column chromatography*. In this technique a suitable adsorbent [Like alumina (Al_2O_3), silica gel (a hydrated form of SiO_2), powdered cellulose, finely divided natural silicates (like keiselguhr), ground glass] is packed in a small glass column and this constitutes stationary phase. The mixture to be separated is taken in a suitable solvent and this solution is poured slowly on the top of the column. As the solution passes through the column, the different components of the mixture get adsorbed (*i.e.*, attached to the surface of the adsorbent) at different levels of the column. The components which are adsorbed very strongly are retained at the top; while the other are adsorbed at lower levels of the column (If the material consists of only one component, it will show only one adsorption band on the column. This is considered as conclusive test for the purity of substance). The number of adsorbed bands formed can be detected

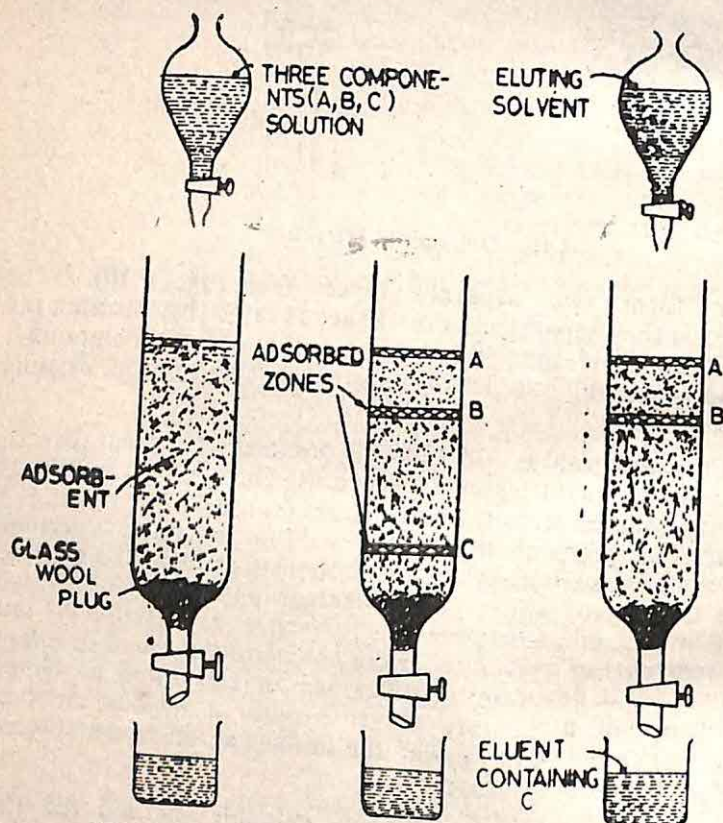


Fig. 4-11. Illustration of column chromatography.

visually if components are coloured. Colourless components may be detected spectrophotometrically. The different adsorbed components are then *eluted* with a selected solvent (mobile phase). The eluent dissolves out the different components from the various adsorbed zones selectively and thus 'work out' the different zones (or bands) in the form of solutions which are collected separately. The eluted liquids from each zone is then distilled off

to get the various components in pure form. The eluent usually employed are petroleum ether, carbon tetrachloride, benzene, alcohol, etc. More than one eluent may be used in certain cases. The principle of column chromatography is illustrated in Fig. 4.11.

4.2. QUALITATIVE ANALYSIS OF ELEMENTS

In the study of any organic compound it is an important step to know the elements present in it. The steps to be followed for determining the percentages of elements in the compound are decided on the basis of its elemental analysis. Fixing of the molecular formula follows next.

The elements ordinarily present in organic substances are carbon, hydrogen, oxygen, nitrogen, sulphur and halogens. Their presence can be tested by the tests detailed below.

(1) Tests for carbon and hydrogen. A dried sample of the organic substance is mixed with dry cupric oxide in the ratio of 1 to 4 and heated in a hard glass test tube (Fig. 4.12). The carbon

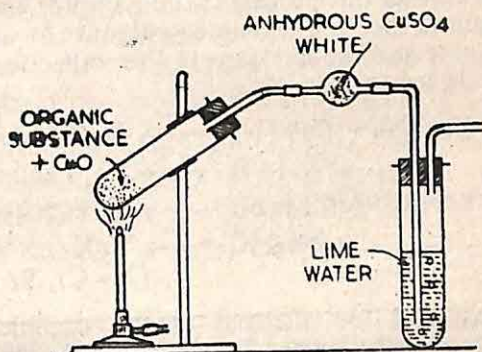
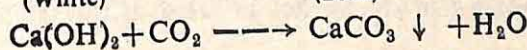


Fig. 4.12. Testing for carbon and hydrogen.

present is oxidised to carbon dioxide and the hydrogen to water vapour.

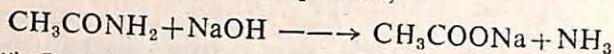


The gaseous products of reaction are passed first over anhydrous copper sulphate powder (white) and then through lime water. If the reaction products contain water vapour, copper sulphate will turn blue and if only carbon dioxide be present, it will not have any effect on copper sulphate but it will turn lime water milky.

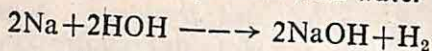


(2) Tests for nitrogen. (i) *Heating with soda-lime.* The substance to be tested is mixed with soda-lime and heated. Active

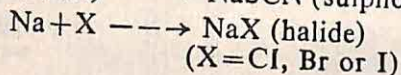
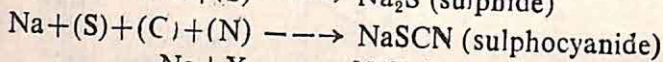
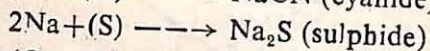
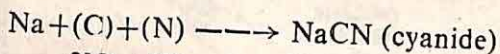
component of soda-lime* is NaOH. If odour of ammonia is observed it indicates the presence of nitrogen. This test is easily given by amides. Some nitrogen compounds do not respond to this test (e.g., nitro and diazo compounds).



(ii) *Lassaigne's test.* For this test a "sodium extract" is prepared from the substance. This is done by heating a pea-sized piece of sodium metal in a combustion tube (5 cm in length and 0.3 cm in dia.) and melted over bunsen burner flame. Organic substance is added to the molten sodium pinch by pinch or drop by drop. After some substance has reacted, the heating of the combustion tube is gradually increased to redness. The red hot tube is broken into about 10 ml of distilled water kept in a dish. The solution is then heated to boiling for a few minutes. Any of the sodium metal, left unreacted, reacts with water as follows.

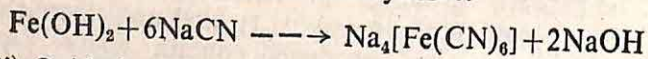


The solution is filtered. The filtered solution is briefly called *sodium extract*. In this process the nitrogen of the organic substance is converted to sodium cyanide, sulphur to sodium sulphide or sulpho cyanide and the halogens to the respective halides. All these are soluble in water.

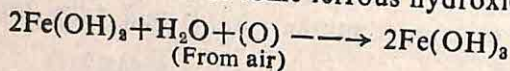


We can test for nitrogen of the organic substance in the sodium extract as follows: Take about 2 ml of the sodium extract in a test tube. Test it with litmus paper. It is expected to be alkaline. If it is not alkaline, make it sufficiently alkaline by adding sodium hydroxide solution. Then, add some ferrous sulphate solution into the test tube. A thick precipitate of ferrous hydroxide is formed. This mixture is boiled for some time. During this boiling two important things happen:

(i) Formation of sodium ferrocyanide.



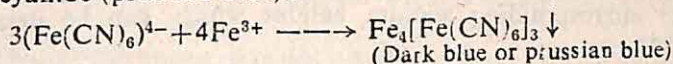
(ii) Oxidation of some ferrous hydroxide to ferric hydroxide.



The mixture is cooled and acidified with dilute sulphuric acid (hydrochloric acid should not be used at this stage). Acidification

Soda-lime is made by shaking quick lime with a solution of caustic soda. It is granular in form and is not deliquescent like caustic soda. It, however, is a strong base and is very efficient for absorbing CO_2 .

converts the ferrous hydroxide to ferrous sulphate, and ferric hydroxide to ferric sulphate. The ferric ions thus formed react with the ferrocyanide ions formed from nitrogen in the original compound to give a blue colloidal solution or precipitate of ferric ferrocyanide (prussian blue).



Notes. (i) Diazo compounds fail to give this test in spite of containing nitrogen. (ii) Organic compounds containing nitrogen and sulphur together may give sodium sulphocyanide in the extract. Above series of steps in that case may give a blood red coloration due to formation of ferric sulphocyanide.

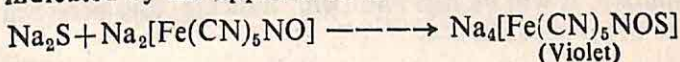


(3) Tests for sulphur. (a) *Lassaing's test.* Sulphur of an organic substance is converted to sodium sulphide during the preparation of sodium extract. This can be easily tested for sulphur as follows :

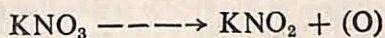
(i) Acidify 2 ml of sodium extract with acetic acid and add lead acetate solution. In the presence of sulphide ions, a black precipitate of PbS is formed.



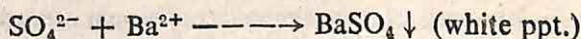
(ii) Mix some freshly prepared sodium nitroprusside solution with 2 ml of alkaline sodium extract. Presence of sulphide is indicated by the appearance of violet colour in the solution.



(b) *Oxidation test.* The organic substance is mixed with the oxidising mixture (consisting of sodium carbonate and potassium nitrate) and fused by heating in a dish. The residue is stirred with water and filtered. The sulphur part of organic compound is present in the filtrate as sulphate ions.



The filtrate is acidified with hydrochloric acid and BaCl_2 solution is added to it. If sulphate be present a white precipitate of BaSO_4 , insoluble in hydrochloric acid is formed.



This test, indicates the presence of sulphur in the organic compound.

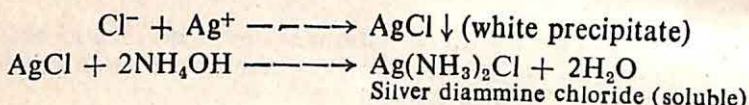
(c) *Carius test.* Above mentioned tests are likely to fail with volatile substances. In that case the Carius test can be carried out. Some of the substance is heated in a sealed thick-walled glass tube with concentrated nitric acid in a closed furnace. The oxidation of the compound occurs and the sulphur part is converted to

sulphuric acid. The tube is cooled and the seal is broken carefully. Presence of H_2SO_4 in the products can be tested with BaCl_2 or $\text{Ba}(\text{NO}_3)_2$ as in the oxidation test described above.

(4) Tests for halogens. (a) *Lassaigne's test*. In the sodium fusion test halogens present in the organic substance are converted to the corresponding sodium halides which can be detected as follows:

(i) *Silver nitrate test*. 2 ml of the sodium extract is boiled with dilute HNO_3 for a few minutes to decompose and destroy the cyanide, sulphide or sulphocyanide, if present (these salts interfere in the testing of halides). The solution is cooled and mixed with AgNO_3 solution. Halides are precipitated as silver halides which are insoluble in nitric acid solution. The precipitate is then characterised as follow ;

If the precipitate of silver halide is *white* and *soluble in ammonium hydroxide solution*, it is of AgCl and indicates the presence of chlorine in the organic substance.

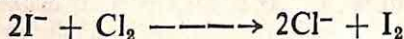


If the precipitate of silver halide is *pale yellow* and *only sparingly soluble in ammonia solution*, it will be of AgBr and will indicate the presence of *bromine* in the organic substance.

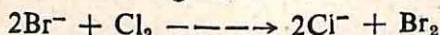
If the precipitate of silver halide is *yellow* and *insoluble in ammonia solution*, it will be AgI and will indicate the presence of *iodine* in the organic substance.

Note. Cyanide, sulphocyanide and sulphide ions must be removed from the sodium extract before adding AgNO_3 as all of these give white precipitates with AgNO_3 which are insoluble in ammonia solution and thus we may have misleading results.

(ii) *Chloroform test*. 2 ml portion of sodium extract is acidified with dilute sulphuric acid. 5 drops of chloroform are added and the mixture is gradually treated with chlorine water and vigorously shaken. The colour of the chloroform layer is watched. Development of *violet colour in chloroform layer* and *yellow colour in aqueous layer* indicates formation of iodine and its presence in the organic substance.



Development of *orange-red colour in chloroform layer* and *yellow colour in aqueous solution* indicates the formation of *bromine* and its presence in the organic substance.



Note. Instead of chloroform, carbon tetrachloride can also be used. Nitric acid or hydrogen peroxide can be used in place of chlorine water.

(b) *Beilstein test*. In this test a clean copper wire is heated in a Bunsen flame till it stops giving green colour to the flame. A

little of the organic substance is put on this copper wire and heated again in the Bunsen flame. If the flame acquires a green colour now, it indicates the presence of some halogen in the organic substance. The halogen forms the volatile copper halide (with the non-volatile copper oxide layer on copper wire) which colours the flame green.

Though this test is very sensitive, it is given by some substances which do not have any halogen in them. Urea is one of such substances.

(5) **Test for oxygen.** We do not have some direct and simple test for this element. If by heating the organic substance in absence of oxygen, we get any oxygen containing products such as water vapour or carbon dioxide, presence of oxygen in the substance can be accepted.

4.3. QUANTITATIVE ANALYSIS OF ELEMENTS

In the analysis of an organic substance, after the detection of elements present, the next step is estimation of elements present in it. We shall now learn in brief how carbon, hydrogen, nitrogen, halogens, sulphur, phosphorus and oxygen are estimated in organic compounds.

(1) **Estimation of carbon and hydrogen (Leibig's combustion method).** Apparatus used is shown in Fig. 4.13. All the parts are labelled. In this method carbon and hydrogen are estimated simul-

BOAT CONTAINING

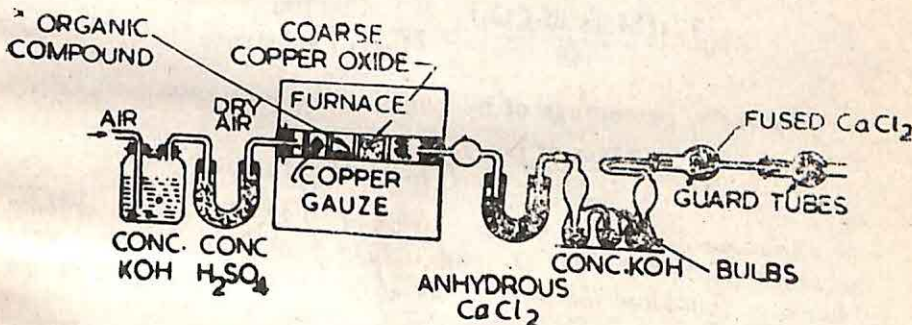


Fig. 4.13. Apparatus for estimation of carbon and hydrogen.

taneously. A known mass of the organic substance (about 0.2 g) is mixed with an excess of cupric oxide powder and heated in a stream of CO_2 -free oxygen. This oxidises carbon to carbon dioxide and hydrogen to water vapour. The stream of gases passes over a heated bed of coarse copper oxide to complete the oxidation. The issuing gases then pass through calcium chloride tube (for absorbing water vapour) and a set of bulbs containing concentrated solution of KOH (for absorbing CO_2). A calcium chloride guard tube at the end prevents atmospheric moisture from being absorbed by the KOH solution.

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Increase in the masses of calcium chloride tube and KOH bulbs measure respectively the masses of H_2O and CO_2 formed by the combustion of the substance. From these mass percentages of carbon and hydrogen in the organic substance can be calculated as follows :

Let mass of substance taken $= w \text{ g}$

Mass of CO_2 formed $= x \text{ g}$

Mass of H_2O formed $= y \text{ g}$

Mass of carbon in 44 g of $\text{CO}_2 = 12 \text{ g}$

\therefore Mass of carbon in $x \text{ g}$ of $\text{CO}_2 = \frac{12x}{44}$

Mass of hydrogen in 18 g of $\text{H}_2\text{O} = 2 \text{ g}$

\therefore Mass of hydrogen in $y \text{ g}$ of $\text{H}_2\text{O} = \frac{2y}{18} \text{ g}$

\therefore Mass of carbon in $w \text{ g}$ of substance $= \frac{12x}{44w} \text{ g}$

or Mass of carbon in 100 g of substance $= \frac{12x}{44w} \times 100 \text{ g}$

Thus, percentage of carbon in the substance,

$$= \frac{12x(\text{Mass of } \text{CO}_2)}{44} \times \frac{100}{\text{Mass of substance}}$$

Similarly, percentage of hydrogen in the substance,

$$= \frac{2y(\text{Mass of } \text{H}_2\text{O})}{18} \times \frac{100}{\text{Mass of substance}}$$

Example 14.1. In the combustion of 0.2100 g of an organic substance 0.1620 g of CO_2 and 0.1215 g of water vapour were obtained. Calculate the percentage of carbon and hydrogen in the substance.

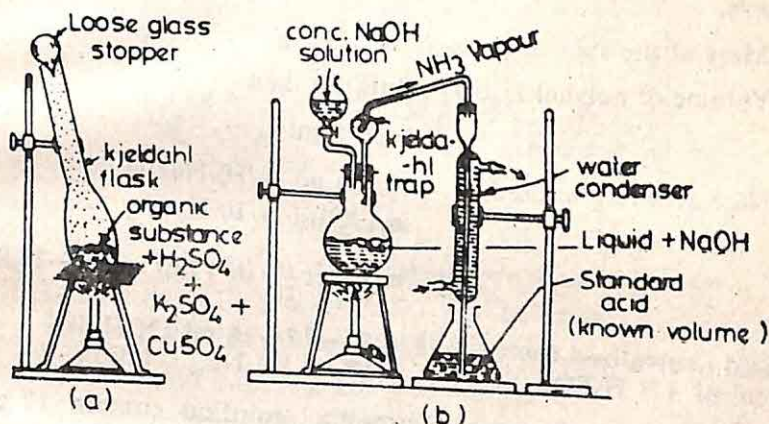
$$\text{Percentage of carbon} = \frac{12 \times 0.162}{44} \times \frac{100}{0.21} = 21.04$$

$$\text{Percentage of hydrogen} = \frac{2 \times 0.1215}{18} \times \frac{100}{0.21} = 6.34.$$

Since the sum of the percentages of carbon and hydrogen is only 66.34, the rest is possibly oxygen or other elements.

(2) **Estimation of nitrogen (Kjeldahl's method).** A known quantity of the substance (about 0.5 g) is mixed with concentrated H_2SO_4 and heated in a long necked pear shaped Kjeldahl flask (Fig. 4.14 a). Some mercuric sulphate (a catalyst for oxidation

of the substance) and some potassium sulphate (to raise the boiling point of sulphuric acid) are also added to the flask. On heating the mixture, carbon (of the compound) is oxidised to CO_2 , hydrogen to H_2O and the nitrogen is converted to ammonium sulphate. The reaction mixture which might have turned black or brown in the beginning due to the formation of carbon clears up at the end. The next step in the estimation is to find out how much ammonium sulphate or ammonia has been formed. For this the strongly acidic mixture from Kjeldahl flask along with the washings is transferred to a round bottom flask. Excess of concentrated NaOH solution then added to this flask whereby ammonium sulphate is converted into ammonia (Fig. 4.14b). The ammonia solution coming out of the



condenser is absorbed in a measured volume of a standard solution of sulphuric acid. The excess of acid left behind after absorption of ammonia is estimated by titration.

Let mass of organic compound taken $= W \text{ g}$
 Volume of standard acid taken $= V \text{ ml of } N_1 \text{ normality}$
 Volume of alkali required for excess acid $= v \text{ ml of } N_1 \text{ normality}$

Now $v \text{ ml of } N_1 \text{ alkali} \equiv v \text{ ml of } N_1 \text{ acid solution}$

\therefore Acid left unused $= (V - v) \text{ ml of } N_1 \text{ normality}$

\therefore But $(V - v) \text{ ml of } N_1 \text{ acid} \equiv (V - v) \text{ ml of } N_1 \text{ ammonia}$

\therefore Ammonia liberated $= (V - v) \text{ ml of } N_1 \text{ normality}$

But 1,000 ml of normal ammonia solution contains 17 g of ammonia or 14 g of nitrogen.

\therefore Amount of nitrogen present in $(V - v) \text{ ml of } \text{NH}_3 \text{ of } N_1$

normality $= \frac{14}{1000} \times (V - v) \times N_1 \text{ g}$

Hence, percentage of nitrogen

$$= \frac{14}{1000} \times (V-v) \times N_1 \times \frac{1}{W} \times 100$$

$$= \frac{1.4 N_1 (V-v)}{W}.$$

Example 4.2. On estimating nitrogen in 1.5240 g of an organic substance by the Kjeldahl method, the ammonia evolved on heating with NaOH solution was absorbed in 30.0 ml of normal sulphuric acid solution. The residual acid required 120.0 ml of N/10 NaOH for neutralization. Calculate the percentage of nitrogen in the organic substance.

Mass of the substance taken = 1.5250 g

Volume of normal H_2SO_4 solution taken

$$= 30.0 \text{ ml}$$

Now acid left unused

$$\equiv 120 \text{ ml N/10 NaOH}$$

$$\equiv 120 \text{ ml N/10 H}_2\text{SO}_4$$

$$\equiv 120 \times \frac{1}{10} \text{ or } 12 \text{ ml of } 1\text{N-H}_2\text{SO}_4$$

\therefore Acid neutralized by
or 18 ml of 1N H_2SO_4

$$\text{NH}_3 = 30 - 12 = 18 \text{ ml } 1\text{N H}_2\text{SO}_4$$

$$= 18 \text{ ml } 1\text{N NH}_3 \text{ solution}$$

But 1,000 ml of normal ammonia solution contain 17 g of ammonia or 14 g nitrogen.

$$\therefore 1,000 \text{ ml } 1\text{N ammonia} \equiv 14 \text{ g nitrogen}$$

$$\therefore 18 \text{ ml } 1\text{N ammonia} \equiv \frac{18}{1000} \times 14 \text{ or } 0.252 \text{ g nitrogen}$$

\therefore nitrogen in 1.525 g of substance

$$= 0.225 \text{ g}$$

or percentage of nitrogen

$$= \frac{0.225}{1.525} \times 100 = 16.5.$$

(3) Estimation of halogen by the Carius method. A small quantity of the substance is weighed in a small ignition tube (3 mm in diameter \times 50 mm in length) and is placed in Carius tube (a thick-walled Jena glass tube about 45 cm long and 2.5 cm in diameter) having enough of concentrated HNO_3 and AgNO_3 crystals (Fig. 4.15 a). The Carius tube is sealed by using an oxygas flame. The sealed tube is placed in an iron socket tube heated in a special furnace. The furnace temperature is maintained near 475K (Fig. 4.15b) for six to seven hours and then the furnace is allowed to cool down to room temperature. The halogen part of the substance is converted into the corresponding silver halide. After breaking the seal, contents of the Carius tube are collected. Silver halide

is filtered, washed, dried and weighed. Percentage of the halogen is then calculated from the mass of silver halide formed.

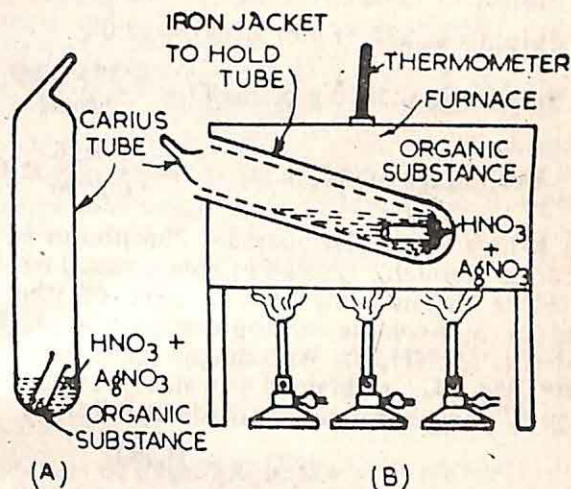


Fig. 4.15. Estimation of halogen by the Carius method.

143.5 g of AgCl contains 35.5 g of chlorine.

188 g of AgBr contains 80 g of bromine.

235 g of AgI contains 127 g of iodine.

Notes. i) The seal on the Carius tube should be strong one. Pressure generated in it during the reaction can be quite high. (ii) Iodine estimations do not give accurate results by this method as AgI formed is slightly soluble in conc. HNO_3 and a part of iodine may be oxidised to HIO_3 and this is not precipitated as AgI .

Example 4.3. In a Carius estimation 0.1890 g of a chloro-compound gave 0.2870 g of AgCl precipitate. Calculate the percentage of chlorine in the compound.

Chlorine in 143.5 g of AgCl = 35.5 g

$$\therefore \text{Chlorine in 0.2870 g of } \text{AgCl} = \frac{0.287}{143.5} \times 35.5 = 0.71 \text{ g}$$

$$\therefore \text{Percentage of chlorine} = \frac{0.71}{0.189} \times 100 = 37.6.$$

(4) **Estimation of sulphur.** This is also done by the Carius method. Instead of adding crystals of AgNO_3 , as done for halogens, crystals of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ are added. The sulphur part is oxidised to sulphuric acid. This gives a precipitate of BaSO_4 which is collected, washed, dried and weighed. 233.34 g of BaSO_4 contains 32 g of sulphur.

Example 4.4. In a Carius estimation 0.2595 g of an organic compound gave 0.3500 g of BaSO_4 precipitate. What is the

percentage of sulphur in the compound: ($Ba=137.34$, $S=32.0$, $O=16.0$).

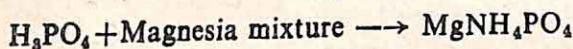
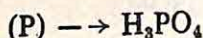
$$\text{Molecular mass of BaSO}_4 = 137.34 + 32.0 + 16.0 = 233.34$$

$$\therefore \text{Sulphur in } 233.34 \text{ g of BaSO}_4 = 32.0 \text{ g}$$

$$\therefore \text{Sulphur in } 0.3500 \text{ g of BaSO}_4 = \frac{0.35 \times 32.0}{233.34} = 0.0496 \text{ g}$$

$$\Delta \text{ Percentage of sulphur} = \frac{0.0496}{0.2596} \times 100 = 18.5.$$

(5) Estimation of phosphorus. Phosphorus is also estimated by the Carius method. Instead of concentrated nitric acid, fuming nitric acid is taken. Phosphorus part of the compound is converted to non-volatile orthophosphoric acid, H_3PO_4 , which is precipitated as $MgNH_4PO_4$ with magnesia mixture. On heating the precipitate $Mg_2P_2O_7$ is obtained as a stable residue. Calculation of percentage of phosphorus can be made as follows:



$$\text{Molecular mass of } Mg_2P_2O_7 = 2 \times 24 + 2 \times 31 + 7 \times 16 = 222 \text{ units.}$$

$$\therefore 222 \text{ g of } Mg_2P_2O_7 \text{ contain } 62 \text{ g of phosphorus}$$

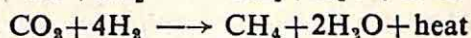
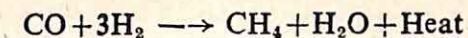
Let mass of substance be w gram and of $Mg_2P_2O_7$ residue be x grams.

$$\therefore \text{Mass of phosphorus in } x \text{ grams of } Mg_2P_2O_7 = \frac{62x}{222} \text{ g}$$

$$\therefore \text{Percentage of phosphorus in the compound} = \frac{62x}{222} \times \frac{100}{w}$$

$$= \frac{100 \times 62}{222} \times \frac{\text{Mass of } Mg_2P_2O_7}{\text{Mass of substance}}$$

(6) Estimation of oxygen. Ordinarily the percentage of oxygen in a compound is estimated by subtracting from 100 the sum of the percentages of other elements directly determined. This estimation is likely to result in some error as it will include the errors in the other estimations which may or may not cancel out. Ter Meulen gave a method for estimating oxygen in a compound directly. In this method a known quantity of the organic substance is heated in a current of dry hydrogen and the resulting gases and vapours are passed over heated *platinised asbestos*. The carbon is converted to CO or CO_2 with the help of oxygen in the compound. These gases are mixed with a further amount of hydrogen and passed over finely divided nickel or thoria (ThO_2) heated to 623K. The oxides of carbon are converted to CH_4 and the oxygen is completely converted to water vapour.



Water vapour is absorbed in a CaCl_2 tube and its increase in mass is found out. Thus, the oxygen present in the substance is estimated directly. This method is followed whenever a doubtful situation about the percentage of oxygen in a compound arises; otherwise the method of difference is adopted.

Example 4.5. From 0.2100 g of an organic substance 0.4620 g of CO_2 and 0.1215 g of H_2O were formed. On heating 0.1040 g of the same substance with caustic soda yielded all its nitrogen as ammonia, neutralization of which needed 15 ml of $\text{N}/20 \text{ H}_2\text{SO}_4$. If oxygen is only other element present in the substance, what is its percentage in the substance?

$$\begin{aligned}\text{Percentage of carbon in the substance} &= 0.462 \times \frac{12}{44} \times \frac{100}{0.21} \\ &= 60.0.\end{aligned}$$

$$\begin{aligned}\text{Percentage of hydrogen in the substance} &= 0.1215 \times \frac{2}{18} \times \frac{100}{0.21} \\ &= 6.43. \\ \text{Now } 17 \text{ g of } \text{NH}_3 &\equiv 14 \text{ g of nitrogen}\end{aligned}$$

\therefore Ammonia evolved on heating with

$$\begin{aligned}\text{NaOH} &= 15 \text{ ml of } \frac{\text{N}}{20} \text{H}_2\text{SO}_4 \\ &= 15 \text{ ml of } \frac{\text{N}}{20} \text{NH}_3 \text{ soln.}\end{aligned}$$

But 1,000 ml of 1N NH_3 soln. \equiv 17 g of NH_3

$$\begin{aligned}\therefore 15 \text{ ml of } \frac{\text{N}}{20} \text{NH}_3 \text{ soln.} &\equiv \frac{14}{1000} \times \frac{1}{20} \times 17 \text{ g of } \text{NH}_3 \\ &= \frac{15 \times 17}{1000 \times 20} \times \frac{14}{17} \text{ g of nitrogen}\end{aligned}$$

\therefore Percentage of nitrogen in the substance

$$= \frac{15 \times 14}{1000 \times 20} \times \frac{100}{0.104} = 10.09.$$

\therefore Sum of percentages of C, H and N

$$= 60.00 + 6.43 + 10.09 = 76.52.$$

\therefore Percentage of oxygen

$$\begin{aligned}&= 100 - 76.52 \\ &= 23.48.\end{aligned}$$

4.4. EMPIRICAL FORMULA

The empirical formula of a substance is derived from the percentage composition of the substance. Such a formula indicates

the simplest whole number ratio of the atoms of elements in a molecule of the substance. However, the molecular formula of a substance must indicate the exact number of atoms of each kind in a molecule of the substance. The molecular formula of a substance is either the same as its empirical formula or a whole number of it. Molecular mass of a substance can be obtained experimentally and this information can be coupled with the empirical formula to arrive at the molecular formula through the relationship :

$$\frac{\text{Molecular formula}}{\text{Empirical formula}} = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

Determination of empirical formula. From the mass composition of a substance, its empirical formula is determined using the following steps :

(i) The percentages of elements are added together ; the sum should be very close to 100.

(ii) The mass percentages of elements are divided by the respective atomic masses to get the ratio of atoms by numbers.

(iii) These numbers are divided by the smallest number amongst them. This gives the simplified ratio by numbers.

(iv) If the ratio numbers at this stage are not whole numbers, they are all multiplied by a suitable number to convert all of them to whole numbers.

(v) These whole numbers are then placed on the right bottom side of the symbols of elements to get the empirical formula of the substance.

The simple example given below illustrates the steps listed above.

Example 4.6. Following percentage figures were obtained on analysis a substance : C=54.5% ; H=9.09%. The remaining element was oxygen. Obtain the empirical formula for the substance.

$$\therefore \text{Percentage of oxygen (by difference)} = 100 - (54.5 + 9.09) \\ = 36.41$$

Element	Percentage	Atomic mass	Relative number of atoms	Dividing by smallest factor	Simple whole number ratio
Carbon	54.50	12	$\frac{54.50}{12} = 4.50$	$\frac{4.54}{2.27} = 2$	2
Hydrogen	9.09	1	$\frac{0.09}{1} = 0.09$	$\frac{9.02}{2.27} = 4$	4
Oxygen	36.41	16	$\frac{36.41}{16} = 2.27$	$\frac{2.27}{2.27} = 1$	1
<hr/> 100.00					

\therefore Empirical formula = C_2H_4O .

4.5. MOLECULAR FORMULA

The exact number of atoms of each kind present in one molecule of a substance are indicated in the molecular formula of the substance. The relationship between the empirical and the molecular formulae of a substance has been given earlier. We can say that :

Molecular formula = $n \times$ Empirical formula

$$\text{or } n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

where n is a whole number. Thus, for finding the molecular formula of a substance we need its molecular mass, which can be determined by using an appropriate method depending on the nature of the substance.

4.6. DETERMINATION OF MOLECULAR MASS

Important methods used for finding molecular mass of organic substance are discuss below :

(1) Victor Meyer method (for volatile substances). In this method a known mass of a volatile liquid (or solid) is evaporated quickly in a Victor Meyer tube maintained at a temperature at least 20° higher than the boiling point of the substance. The vapour so formed pushes out an equivalent volume of air from the upper parts of the tube. The displaced air is collected in the graduated tube and its volume, temperature and pressure are noted. Apparatus used is shown in Fig. 4.16. The major part of the set up is the Victor Meyer tube. It has a cylindrical bulb of about 50 to 75 ml capacity, a side tube for the exist of displaced air and a cup at the top with a well-fitting rubber cork. A pad of some shock absorbing non reactive material such as sand, glass wool or asbestos fibres is kept in the Victor Meyer tube. Other parts of apparatus are the outer heating jacket for Victor Meyer tube, collection unit for displaced air and the Hoffmann's bottle.

The Victor Meyer tube is set in an outer jacket (made of metal or glass). Enough of bath liquid (generally water) is placed

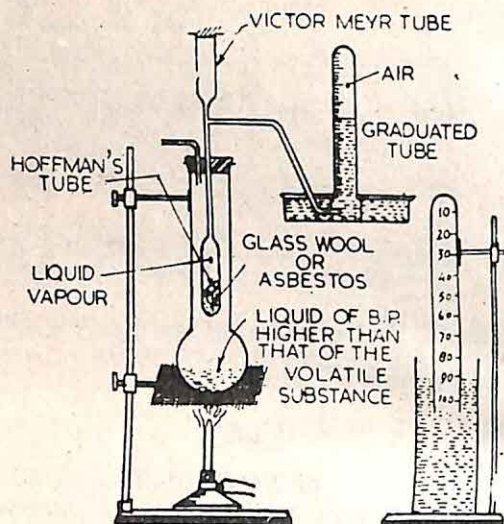


Fig. 4*16. Victor Meyer's method.

in the jacket. A burner is placed below the jacket and the heating is started. The side arm of Victor Meyer tube is connected to the graduated gas measuring tube. During the initial heating, the cork at the top of Victor Meyer tube is kept loose to allow an escape of the expanding air as the tube gets heated up. While the tube is being heated to the constant temperature of the boiling bath liquid about 0.100 g of the substance, whose molecular mass is to be measured, is accurately weighed in a Hoffmann's bottle. (Hoffmann's bottle is kept in a closed container till it is needed for being dropped into Victor Meyer's tube). When steam has been issuing for about 15 minutes from the top of the jacket, the top cork on the Victor Meyer tube is closed hard and level in the gas measuring tube is watched. If it does not fall for about 5 minutes, it is assumed that Victor Meyer tube and the air in it have acquired the steady temperature. The water level in the gas measuring tube is noted. After this the following operations are carried out in quick succession :

- (i) The cork on top of Victor Meyer tube is loosened.
- (ii) The stopper on the Hoffmann's bottle is turned to make its motion free.
- (iii) The top cork on Victor Meyer tube is lifted momentarily. Hoffmann's bottle is dropped in and the cork closed hard.

As soon as the Hoffmann's bottle reaches the pad on the bottom of Victor Meyer tube, the temperature of the liquid in it is suddenly raised to well above its boiling point. The liquid evaporates quickly and pushes out an equivalent volume of air

from Victor Meyer's tube. This displaced air is collected in the gas collection unit. When no more air is pushed out for five minutes, the stop-cock on the gas measuring tube is closed. The displaced air in the gas measuring tube is allowed to acquire the temperature of water in it. The volume, temperature and pressure of the displaced air are measured and a correction is made in the pressure of air for the aqueous tension.

Let mass of liquid in Hoffmann's bottle = w g.

Volume of displaced air *after correction* = v ml.

Temperature of collected air (water temperature)

$$= T \text{ K}$$

Pressure (Barometric) = p torr.

Aqueous tension at T K = p' torr.

\therefore Corrected pressure for displaced air (dry) = $(p - p')$ torr.

The volume of air displaced is reduced to STP with the help of gas equation. Let this volume at STP be V ml.

A. V ml of air is displaced by = w g of substance

or 22,400 ml of air is displaced by = $\frac{22,400 \times w}{V}$ g

Hence, molecular mass = $\frac{w \times 22,400}{V}$.

Example 4.7. In a Victor Meyer experiment 0.100 g of a liquid on evaporation gave 25.0 ml of displaced air. The water temperature in the gas measuring tube was 293 K and the barometer reading was 750 torr. Aqueous tension at 293 K equals 17.4 torr. Calculate the molecular mass of the liquid.

Here mass of liquid, $w = 0.1$ g ; $P_1 = 750 - 17.4 = 732.6$ torr ;
 $V_1 = 25.0$ ml ; $T_1 = 293$ K ; T_2 (at STP) = 273 K ; $P_2 = 760$ torr ;
 $V_2 = ?$

But

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \frac{732.6 \times 25}{293} = \frac{760 \times V_2}{273}$$

\therefore

$$\therefore \text{Volume at STP, } V_2 = \frac{273 \times 732.6 \times 25}{293 \times 760}$$

$$= 22.46 \text{ ml or } 0.02246 \text{ litre.}$$

\therefore Mass of 0.02246 litre at STP of vapour = 0.100 g.

$$\begin{aligned}\text{or mass of 22.4 litres at STP of vapour} &= \frac{22.4}{0.02246} \times 0.100 \\ &= 99.95 \text{ g.}\end{aligned}$$

$$\text{Hence molecular mass of liquid} = 99.95.$$

(2) **Volumetric Methods (for acids and bases).** In this method a known quantity of the substance is dissolved in distilled water or neutral alcohol and the solution is made up to a known volume. A measured volume of this acid (or base) solution is then titrated against a standard solution of strong alkali (or acid) as required using an appropriate indicator (phenolphthalein or methyl orange). From the titre value of the prepared solution, chemical equivalent of the solute can be calculated. Knowing the acidity (in case of a base) or basicity (in case of an acid) molecular mass can be obtained.

Assuming that a measured volume of an acid solution containing w gram of the acid can be neutralized by V ml of x N = NaOH solution, then

$$V \text{ ml of } x \text{ N-NaOH} \equiv w \text{ gram of acid}$$

$$\text{or } 1 \text{ ml of } x \text{ N-NaOH} \equiv \frac{w}{V} \text{ gram of acid}$$

$$\therefore 1000 \text{ ml of } 1 \text{ N-NaOH} \equiv \frac{w}{V} \times \frac{1000}{x} \text{ gram of acid}$$

$$\text{or } 1 \text{ g equivalent of NaOH} \equiv \frac{1000 w}{Vx} \text{ gram of acid}$$

$$\therefore 1 \text{ g equivalent of acid} = \frac{1000 w}{Vx} \text{ gram of acid}$$

If the basicity of acid is n ,

$$\therefore \text{Molecular mass of acid} = \frac{1000 w}{Vx} \times n$$

Molecular mass of a base can be calculated in a similar manner.

Example 4.8. On combustion 0.200 g of a monobasic organic acid gave 0.505 g CO_2 and 0.0892 g water. For neutralizing 0.183 g of the acid dissolved in water 15 ml of $N/10$ NaOH were required. Obtain the molecular mass and the molecular formula of the acid.

$$\text{Percentage of carbon in the acid} = \frac{12}{44} \times 0.505 \times \frac{100}{0.2} = 68.86$$

$$\text{Percentage of hydrogen in the acid} = \frac{2}{18} \times 0.0892 \times \frac{100}{0.2} = 4.95$$

$$\begin{aligned}\text{Percentage of oxygen (by difference)} &= 100 - (68.86 + 4.95) \\ &= 26.19.\end{aligned}$$

Element	Percentage	Atomic mass	Relative number of atoms	Dividing by smallest ratio	Simple whole number ratio
Carbon	68.86	12	5.74	$\frac{5.74}{1.64} = 3.5$	7
Hydrogen	4.95	1	4.95	$\frac{4.95}{1.64} = 3.0$	6
Oxygen	26.19	16	1.64	$\frac{1.64}{1.64} = 1.0$	2

∴ Empirical formula of acid = $C_7H_6O_2$.

Now 15 ml of $\frac{N}{10}$ or 0.1N-NaOH \equiv 0.183 g of acid.

1000 ml of N-NaOH $\equiv \frac{0.183 \times 1000}{15 \times 0.1} = 122$ g of acid.
 or chemical equivalent of acid = 122 g.

∴ Molecular mass = chemical equivalent \times basicity of acid
 $= 122 \times 1 = 122$

∴ Molecular formula = $\frac{\text{Empirical formula} \times \text{Molecular mass}}{\text{Empirical formula mass}}$

$$= C_7H_6O_2 \times \frac{122}{84 + 6 + 32}$$

$$= (C_7H_6O_2) \times 1$$



(3) Gravimetric method. If we know the *basicity* of an acid or the *acidity* of a base we can find the *molecular mass of the acid* by the *silver salt method* and of the base by *chloroplatinate method*. These are described below.

(a) *Silver salt method for organic acids.* Most organic acids give insoluble silver salts. For making such a silver salt, the acid is dissolved in an excess of ammonia solution to form the ammonium salt solution. The excess of ammonia is expelled by boiling the solution. To the almost neutral salt solution of the acid, silver nitrate solution is added in slight excess to precipitate the silver salt of the acid. The precipitate is filtered, washed and dried. A known quantity of the dry salt is taken in a silica crucible and heated first gradually. A number of salts are charred in this step and some others tend to explode also. After a preliminary decomposition the temperature of the crucible is raised and contents heated to a constant mass. From the mass of silver residue the molecular mass of acid is calculated.

Let us suppose that an equivalent of the acid which provides one hydrogen ion can be represented by RCOOH . The corresponding equivalent of silver salt can be represented by RCOOAg . It is known that chemical equivalent of hydrogen ion is one and of silver ion and silver is 108.

If E stands for the chemical equivalent of acid, RCOOH .

\therefore Chemical equivalent of acid anion $(\text{RCOO})^- = E - 1$.

or Chemical equivalent of silver salt $= (E - 1) + 108 = E + 107$

$$\begin{aligned} \text{But } \frac{\text{Mass of silver salt}}{\text{Mass of silver residue}} &= \frac{\text{Chemical equivalent of silver salt}}{\text{Chemical equivalent of silver}} \\ &= \frac{E + 107}{108} \end{aligned}$$

From the above relationship chemical equivalent of the acid can be calculated. Then,

Molecular mass of acid = Chemical equivalent \times Basicity

Example 4.9. An organic acid is dibasic. 0.456 g of its silver salt leaves behind a residue of 0.324 g of silver. Calculate the molecular mass of the acid.

Let E be the equivalent weight of the acid. Then,

$$\frac{\text{Mass of silver salt}}{\text{Mass of silver residue}} = \frac{\text{Chemical equivalent of silver salt}}{\text{Chemical equivalent of silver}}$$

$$\therefore \frac{0.456}{0.324} = \frac{(E - 1) + 108}{108}$$

$$\text{or } E = \frac{108 \times 0.456}{0.324} - 107 = 45.0.$$

Hence, molecular mass $= E \times 2 = 45.0 \times 2 = 90$.

(b) *Chloroplatinate method for organic bases.* When platinum chloride (PtCl_4) is dissolved in hydrochloric acid it forms chloroplatinic acid (H_2PtCl_6) which is a dibasic acid. It can form with two molecules of mono acid bases insoluble crystalline salts. The salts are called chloroplatinates of bases or platinichlorides of bases. After precipitation the salt is well washed (to remove the impurities of H_2PtCl_6 and HCl) and then dried. A known mass of the salt is ignited in a crucible. The final residue is of platinum metal. Its mass is found out.

If B stands for one equivalent of a base, the formula for the base chloroplatinate will be $\text{B}_2\text{H}_2\text{PtCl}_6$.

Let the mass of the dry salt be W gram and the mass of the residue of platinum be w gram. We may indicate one equivalent of the base by B and a molecule of the base salt by $\text{B}_2\text{H}_2\text{PtCl}_6$.

$$\therefore \text{Formula mass of base salt} = 2B + 2 + 195 + 6 \times 35.5 \\ = 2B + 410$$

But one formula mass of base salt gives one atom of platinum.

$$\therefore \frac{\text{Formula mass of chloroplatinate}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of chloroplatinate}}{\text{Mass of platinum residue}}$$

$$\text{or} \quad \frac{2B + 410}{195} = \frac{W}{w}$$

$$\text{or} \quad 2B = \frac{195 W}{w} - 410$$

$$B = \frac{195 W}{2 w} - 205$$

$$\therefore \text{Molecular mass of base} = B \times \text{Acidity}.$$

Example 4.10. A base is diacidic. 0.98 g of its chloroplatinate on heating left a residue of 0.39 g of platinum. What is the molecular mass of the base?

$$\frac{\text{Formula mass of base chloroplatinate}}{\text{Atomic mass of platinum}} = \frac{\text{Mass of chloroplatinate}}{\text{Mass of platinum}}$$

$$\text{or} \quad \frac{2B + 410}{195} = \frac{0.98}{0.39}$$

$$2B = 195 \times \frac{0.98}{0.39} - 410 = 80$$

$$B = \frac{80}{2} = 40.$$

$$\text{Hence, molecular mass} = B \times \text{acidity} \\ = 40 \times 2 = 80.$$

4.7. MOLECULAR FORMULA OF HYDROCARBON GASES

Molecular formulae for gaseous hydrocarbons can be found out by exploding a known volume of the gas with an oxygen and carrying out the measurements of volumes of gases involved. A graduated gas measuring tube used in these experiments and is called an *eudiometer tube*, which is like an inverted graduated tube. Two platinum wires are fused near the top of it to cause electric sparking for inducing reactions. The tube is filled with a liquid (usually mercury) and a known volume of hydrocarbon gas under examination is drawn into the tube by allowing the liquid to run out. Then, a known excess volume of oxygen is also drawn into the tube. On passing an electric spark in the mixture of gases

at the platinum wire electrodes, gases react. Carbon of hydrocarbon forms CO_2 ; while the hydrogen forms water vapour. The tube is allowed to cool down to initial temperature and the volume of residual mixture of gases is measured. The CO_2 is then absorbed

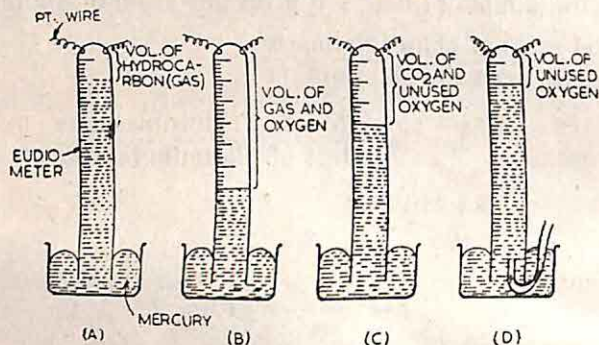
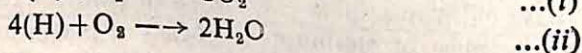
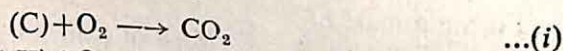


Fig. 4.17. Determination of molecular formula of hydrocarbon.

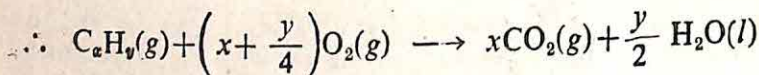
in a solution of caustic potash and the volume of remaining gas, which is oxygen, is also measured. Calculations for arriving at the molecular formula of the hydrocarbon are carried out according to the following plan.

Plan of calculations. The explosion of hydrocarbon with oxygen involves the following reactions.



Thus, we note from equation (i) that for every atom of carbon in the hydrocarbon molecule, one molecule of O_2 is taken up and one molecule of CO_2 is formed. From equation (ii) we note that for every four atoms of hydrogen in the hydrocarbon molecule, one molecule of oxygen is used to form two molecules of water vapour. At room temperature, most of this vapour condenses to liquid water and its volume can be ignored, since it will be negligibly small.

Let us assume that the formula for the hydrocarbon molecule is C_xH_y . Then, x atoms of carbon will need x molecules of O_2 and will form x molecules of CO_2 . The y atoms of hydrogen will need $y/4$ molecules of O_2 to form water.



Experiments are conducted in two ways :

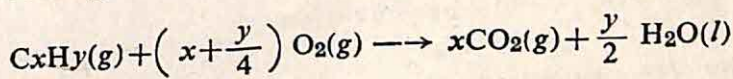
(i) The initial volume of oxygen added and the volumes of mixtures of gases at different steps are known

(ii) The initial volume of oxygen is not known but the volumes of mixtures of gases at different steps are known.

Calculations to be followed are illustrated in the following examples.

Example 4-11. 12 ml of hydrocarbon gas were mixed with 90 ml of oxygen in a eudiometer tube and exploded. On cooling after the explosion, residual mixture of gases had a volume of 72 ml. On adding KOH solution to the mixture, the volume of the gases was reduced by 36 ml and only O_2 was left behind. All volume measurements were at the same temperature and pressure. Calculate the molecular formula for the hydrocarbon.

Let the required molecular formula be C_xH_y . 12 ml of this gas were taken and water vapour will occupy negligible volume after cooling.



$$\therefore 12 \text{ ml} + 12\left(x + \frac{y}{4}\right) \text{ ml} = 12x \text{ ml}$$

$$\therefore \text{Carbon dioxide formed} = 12x \text{ ml}$$

$$\text{and Oxygen used up} = 12\left(x + \frac{y}{4}\right) \text{ ml}$$

Since reduction in gas volume on adding KOH is due to absorption of CO_2 .

$$\therefore \text{Volume of } CO_2 \text{ formed} = 36 \text{ ml}$$

$$\text{and Volume of } O_2 \text{ left unused} = 72 - 36 = 36 \text{ ml}$$

$$\therefore \text{Volume of } O_2 \text{ used up in reaction} = 90 - 36 = 54 \text{ ml}$$

$$\text{Accordingly ; } 12x = 36 \quad \text{or} \quad x = 3$$

$$\text{But} \quad 12\left(x + \frac{y}{4}\right) = 54$$

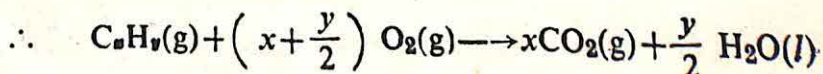
$$\text{or} \quad 3y = 54 - 12x = 54 - 36 = 18$$

$$\therefore y = 6$$

Hence, molecular formula of the hydrocarbon is C_3H_6 .

Example 4-12. When 20 ml of a gaseous hydrocarbon was mixed with excess of oxygen and exploded, there was a reduction in volume of 30 ml. Adding KOH solution caused a further reduction of 40 ml in the volume. All volumes were measured at the same temperature and pressure. Calculate the molecular formula for the gas.

Let the required molecular formula be C_xH_y



$$\text{Now volume of hydrocarbon used} = 20 \text{ ml}$$

$$\text{and volume of } CO_2 \text{ expected to be formed} = 20x \text{ ml}$$

∴ volume of O_2 expected to be used up in reaction

$$= 20 \left(x - \frac{y}{4} \right) \text{ ml.}$$

∴ Expected decrease in volume of gas mixture, after explosion assuming that water vapour condenses, will be

$$= \text{Volume of (hydrocarbon + oxygen used up - } CO_2 \text{ formed)}$$

$$= 20 + 20 \left(x + \frac{y}{4} \right) - 20x$$

$$= 20 + 20x + 5y - 20x$$

$$= 20 + 5y$$

But from actual measurement we have :

Reduction in volume on adding $KOH = 40 \text{ ml}$

and volume of CO_2 formed $= 40 \text{ ml}$

$$\therefore 20x = 40 \text{ or } x = 2$$

Also observed decrease in gas volume after explosion is 30 ml.

$$\therefore 20 + 5y = 30 \text{ or } y = 2$$

Hence, molecular formula for the hydrocarbon $= C_2H_2$.

QUESTIONS

(A) Essay Type

1. By what tests is the purity of an organic substance checked ?
2. How may an organic substance be separated from a mixture of organic and inorganic substances ?
3. Describe some methods for the separation of similar substance from mixtures.
4. How are the components of a liquid mixture separated ?
5. Explain the process of "fractional distillation" and "steam distillation" stating the principles on which they are based.
6. Describe the general methods of purification of liquids.
7. How can we show the presence of carbon, hydrogen, and oxygen in an organic substance ?
8. Describe the detection of nitrogen, sulphur and iodine in an organic substance giving equations where ever possible.
9. Describe the test for halogens in organic compounds.
10. Why can the presence of nitrogen in a substance interfere with the detection of halogens in it ?
11. Describe, giving an outline diagram, Kjeldahl's method of estimating nitrogen.
12. How are carbon, and hydrogen determined quantitatively in organic compounds ?
13. Describe the various methods of estimating halogens in organic compounds.

(B) Short Answer Type

14. How will you test the presence of nitrogen in an organic substance ?
15. What is chloroform test for halogens ?
16. What are the advantages of low pressure distillation ?
17. Write a note on chromatography ?
18. What is the use of a vacuum pump in distillation process ?
19. What is the use of fractionating column ?

(C) Objective Type

20. Put tick marks for the correct answer.

(i) The first organic compound synthesized by Wholer in a chemical laboratory happens to be (a) methane, (b) ethyl alcohol, (c) urea, (d) ethylene.

(ii) The empirical formula of an organic compound of the molecular formula $C_6H_{12}O_6$ will be—(a) CH_2O , (b) $C_2H_4O_2$, (c) $C_6(OH)_6$, (d) $C_6H_{12}O_6$.

(iii) The structural formula of an organic compound represents (a) its composition; (b) its characteristics; (c) the nature of the functional group; (d) the arrangement of atoms in the molecule.

(iv) Substances which volatilise without melting are best purified by (a) steam distillation; (b) crystallisation; (c) sublimation; (d) decantation.

(v) Victor-Meyer's method is used for the determination of vapour densities of (a) inorganic compounds, (b) water soluble compounds, (c) volatile substances; (d) non-volatile substances.

(vi) Lassaigne's test is used to detect the presence of (a) nitrogen in organic compounds; (b) sulphur in organic compounds; (c) nitrogen and sulphur both in the organic compounds; (d) halogens in organic compounds.

(D) Problems

21. *Estimation of Elements.* On reacting 0.185 gram of a substance with concentrated nitric acid and silver nitrate 0.319 gram of silver bromide was formed. Calculate the percentage of bromine in the substance. (Ans. 73.14%)

22. On heating 0.3465 g of a substance with concentrated sulphuric acid and subsequent heating the resulting solution with caustic soda, ammonia was evolved. This ammonia was absorbed in 50 ml of $N-H_2SO_4$. The solution was made upto one litre with distilled water 25 ml of this new solution needed 11.45 ml of $N/10-NaOH$ for neutralization. Calculate the percentages of nitrogen in the compound. (Ans. 17.3%)

23. On combustion of 0.1668 g of an organic compound 0.454 g of CO_2 and 0.0668 g of water formed. On heating 0.1245 g of the same compound with concentrated nitric acid and adding $BaCl_2$ 0.1292 g of $BaSO_4$ was precipitated. Calculate the percentages of elements present in the compound. (Ans. C = 74.22%; H = 4.22%; S = 14.23%; O = 7.11%)

24. Following data was obtained on analysis of an organic substance :

(a) 0.118 g of the substance gave 0.264 g CO_2 and 0.162 g water.

(b) 0.177 g of substance yielded at 293 K and 760 mm Hg pressure 63.1 mm of nitrogen gas.

Calculate the percentage of elements in the compound.

(Ans. C = 61%; H = 15.23%; N = 23.75%)

25. An organic substance has carbon, hydrogen, nitrogen and oxygen. 0.135 g of the substance on combustion gave 0.198 g CO_2 and 3.108 g water. 0.135 g of the substance also give 16.8 ml of nitrogen at STP. Calculate the empirical formula for the substance. (Ans. $C_3H_8NO_2$)

26. 0.118 g of an organic substance gave 0.264 of CO_2 and 0.026 g of water. From 0.177 g of the substance 36.1 ml of dry nitrogen measured at 293 K and 760 mm Hg pressure was obtained. Calculate the empirical formula for the substance. (Ans. $\text{C}_3\text{H}_9\text{N}$)

27. A volatile organic liquid when subjected to Victor Meyer's experiment gave 21.9 ml at 289 K and 753.5 mm Hg pressure of displaced air from 0.0926 g of the liquid. Calculate the vapour density and molecular mass of the liquid. [Ans. (i) 38.31, (ii) 76.62]

28. 0.1008 g of chloroform in a Victor Meyer experiment, on vaporisation displaced 20 ml at 288 K and 757 mm Hg of air. Calculate the molecular mass of chloroform. (Ans. 119.57)

29. In Victor Meyer's method 0.162 g of a volatile liquid on vaporisation displaced 35.0 ml of air measured at 296 K and 745 mm pressure. Vapour pressure of water at 296 K is 25 mm and 1 ml of hydrogen at STP weighs 0.00009 g. (Ans. 117.7)

30. 0.272 g of a monobasic acid required 20 ml of N/10 NaOH solution for neutralization. Calculate the molecular mass of the acid. (Ans. 136.0)

31. 0.083 g of a dibasic acid required 10 ml of N/10 NaOH solution for complete neutralization. Calculate the molecular mass of the acid. (Ans. 166.0)

32. For neutralizing 0.2709 g of a monobasic organic acid 52.2 ml of N/12 NaOH solution is used. What is the molecular mass of the acid? (Ans. 62.3)

33. The silver residue obtained on ignition 0.2214 g of the silver salt of a dibasic acid was 0.144 g. Calculate the molecular mass of the acid. (Ans. 118.0)

34. 0.900 g of the silver salt of a monobasic acid left behind 0.581 g of silver on ignition. What is the molecular mass of the acid? (Ans. 120.6)

35. 0.126 g of pure silver were left behind when 0.3320 g of the silver salt of a dibasic organic acid was heated strongly to a constant weight. Calculate the molecular mass of the acid. (Ans. 118.0)

36. An organic acid is found to be dibasic. 0.500 g of its silver salt on ignition leaves behind 0.325 g of silver. Calculate the molecular mass of the acid. (Ans. 149.0)

37. The chloroplatinate of a diacid base was prepared 0.3663 g of this salt on ignition left behind 0.1015 of platinum. Calculate the molecular mass of the base. (Ans. 294.0)

38. 0.532 g of the chloroplatinate of a diacid base gave on ignition 0.195 g of platinum. What is the molecular mass of base? (Ans. 122.0)

39. Of a monoacid organic base, its platinichloride contained 36.93 per cent platinum. Calculate the molecular mass of the base. (Ans. 118.3)

40. 10 ml of hydrocarbon gas were mixed with 30 ml of oxygen and exploded. Volume of gaseous mixture after explosion was 20 ml. On shaking this mixture with KOH solution, the decrease in volume was 10 ml. Calculate the molecular formula for the hydrocarbon. (Ans. CH_4)

41. On exploding 20 ml of gaseous hydrocarbon with 65 ml of oxygen 56 ml of gaseous mixture were left behind. On shaking it with a KOH solution only 16 ml were left undissolved and this gas was oxygen. Obtain the molecular formula of the hydrocarbon. (Ans. C_2H_2)

